REPORT DOCUMENTATION

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1992	THESIS/DISSERTATION

4. TITLE AND SUBTITLE
In-Situ Biological Reclamation of Contaminated Ground Water

5. FUNDING NUMBERS

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
AFIT Student Attending: Georgia Institute of Technology

8. PERFORMING ORGANIZATION REPORT NUMBER
AFIT/CI/CIA-92-033

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFIT/CI
Wright-Patterson AFB OH 45433-6583

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release IAW 190-1
Distributed Unlimited
ERNEST A. HAYGOOD, Captain, USAF
Executive Officer

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

14. SUBJECT TERMS	15. NUMBER OF PAGES: 127
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

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In-Situ Biological Reclamation of Contaminated Ground Water

A Special Research Problem
Presented to
The Faculty of the School of Civil Engineering

By

Robert L. Fant

In Partial Fulfillment
of the Requirements for the Degree of
Master of Science in Environmental Engineering

Georgia Institute of Technology

ABSTRACT

Four triaxial permeability devices were designed and constructed for use in the Environmental Engineering Department at the Georgia Institute of Technology. These devices were used to determine how time and changing permeants affected a soil sample's hydraulic conductivity. Also the attenuation of the priority pollutant, 2,4-dichlorophenol, was studied. Two areas were looked at concerning attenuation, microbial degradation and adsorption. Microbes were grown in the laboratory and then placed into the soil samples. A permeant containing the pollutant, an oxidant, and nutrients was then passed through the soil sample with the microbes. The effects on the effluent concentration were then studied. Two breakthrough curves and two isotherm tests were run in an attempt to distinguish between microbial decay and adsorptive attenuation. Results of the attenuation studies unfortunately were inconclusive, but valuable knowledge was gained on the operation of and experimental procedures with the triaxial permeability devices.

ACKNOWLEDGEMENT

I want to express my sincere appreciation to my advisor Dr. F. Michael Saunders. He always offered encouragement when things seemed at their worst. I want to thank Dr. Neil Williams and Rich Reid for their invaluable assistance while I constructed the four triaxial cells. I also would like to think Dr. Ed Chian who gave me a kind word when I needed it most. Thank you all.

DEDICATION

I wish to dedicate this project to my wife, Eileen, who encouraged me every step of the way, my sons, David and Jonathan, who are an endless source of inspiration, and my God and King, who makes all things possible.

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Ground Water Fundamentals, Remedial Technology and Research Efforts

Ground-Water Problems

Ground water represents 96%[1] of the available fresh water supply in the United States of America. With fully 50 times[1] the amount of surface water, ground water keeps 117 million Americans and their industries going on a daily basis.[2] Ground water is a critical natural resource.

Estimates indicate that 2% of the total ground water volume is severely contaminated and this includes several single-source aquifers that serve large metropolitan areas.[3] The contamination has been identified as synthetic organic chemicals (SOCs). SOCs have been found in 28% of ground-water systems serving more than 10,000 people and in 17% of systems serving less than 10,000 people.[3] Unfortunately because of time and expense, no survey has been conducted on the thousands of private wells across the country.

Since the 1940s, the number of SOCs has exploded to a level of approximately 65,000 chemicals in common use with 500 to 1000 being added every year.[4] SOCs include chemicals ranging from household cleaners and chemicals used in the plastics industry to pesticides. The proliferation of SOCs has created tremendous problems with the storage, handling, and disposal of these chemicals. The health and environmental effects of all these chemicals have only begun to be studied.

SOCs affect ground water because of poor methods used to dispose of them. Two broad categories of disposal sources, waste and non-waste, that can and do contribute to the ground-water contamination problem are defined

in Table 1-1. Waste disposal sources contain the disgarded refuse of home and industry. Non-waste disposal sources originate from use of, storage of, and exploration for products that provide some of the necessities of life. For instance, the petroleum industry and its exploratory efforts not only produces the gasoline needed to run automobiles, but it also produces taken-for-granted plastic products. Over application of chemicals that are required to grow inexpensive food has become a serious environmental problem, and wells that once provided water for agriculture and domestic use have now become conduits for ground-water contamination.

Of the sources listed below, the one receiving the greatest amount of attention is underground storage tanks. Estimates indicate there are 1.5 to 2.0 million underground tanks in use. The average age of these

Table 1-1: SOC Ground-Water Contamination Sources[2]

Waste Disposal Sources	Non-Waste Disposal Sources
Landfills, Surface Impoundments, Dumps	Abandoned Wells
On-Site Waste Water Disposal System	Accidental Spills
Land Treatment of Municipal and Industrial Wastes	Over Application of Agricultural Chemicals
Land Application of Sludges	Petroleum Exploration and Development
Underground Injection Wells	Above and Below Ground Storage Tanks

tanks was found to be in excess of 16 years. The vast majority of the tanks in use, approximately 1.2 million, are made of carbon steel, the most susceptible to corrosion. Nationwide it is speculated that a total of 75,000 to 100,000 of these tanks are leaking and the number is increasing.[5]

Gasoline migrating from leaking tanks into ground water has caused alarm across the country. Every town in America has a gas station with underground tanks. If drawn from underground sources, the possibility of a town's water supply being contaminated is very real. Large gasoline leaks such as from 30,000 gallon tanks in Northglenn, Colorado and Lee, Maine, rendered the water supplies for these towns completely undrinkable. However, these large leaks could fall into obscurity if the extent of all of the undetectable small leaks could be determined. Jack Raven, EPA's Assisstant Administrator for Water, stated that a leak of "one gallon of gasoline per day leaking into a ground-water source is enough to pollute the water of a 50,000-person community to a level of 100 parts per million."[5] Even at a few parts per million of gasoline, taste and odor can be noticed.[5]

The problem of gasoline and other SOCs leaking into the nation's ground water will be a very difficult one to solve. Engineers, scientists, industry experts, and lawmakers have failed to arrive at a concensus concerning the total scope of the leaking tank problem. No one knows exactly how many tanks are buried, how many of them are leaking, how long the tanks have been leaking, nor what is in them. In order to more fully understand the ground-water pollution problem and some of the possible solutions, a review of basic ground-water concepts and definitions is warranted.[1]

Basic Ground-Water Concepts and Definitions

Ground water is simply water found below the surface of the ground. Since ground water represents 96%[1] of the available fresh water supply in

the United States, it also plays a large part in the hydrologic cycle. The part ground water plays in the hydrologic cycle is shown in Figure 1-1.

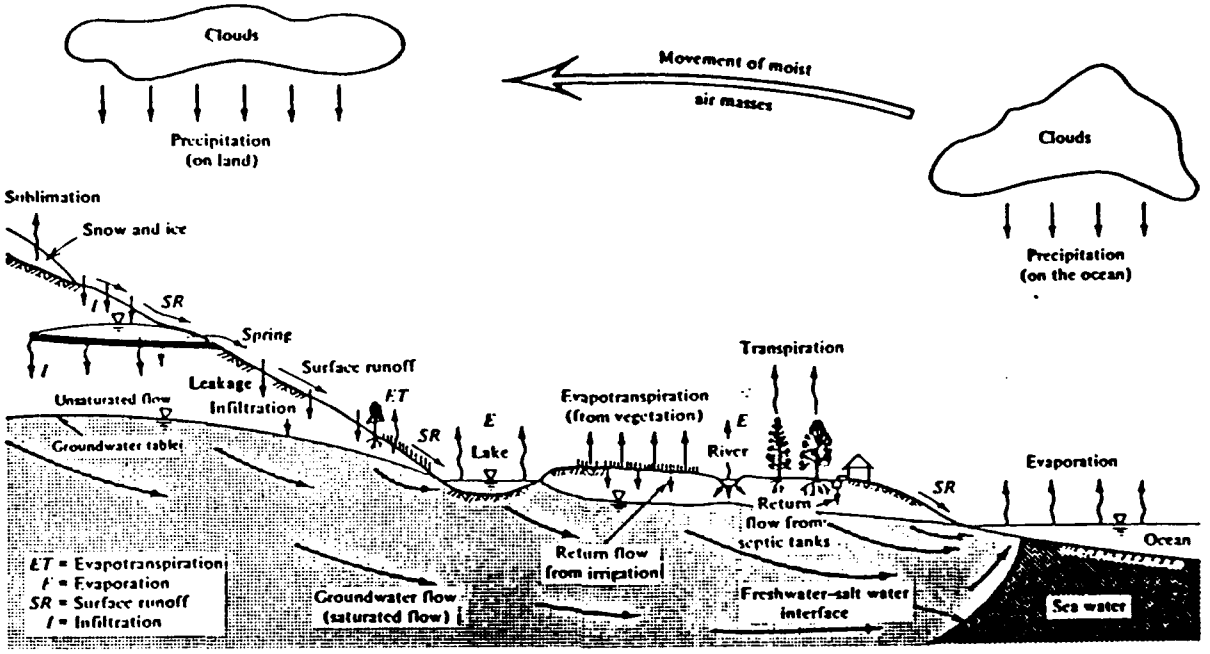


Figure 1-1: Hydrologic Cycle[6]

Four basic underground formations can be related to the storage and transmission of water. First the aquifer, capable of storing and transmitting large quantities of water, contributes most in the way of ground water. Aquifer literally means "water bearing". Other terms that have been used to describe aquifers include ground-water reservoir and water bearing zone. Next, an aquitard transmits water at very low rates as compared to an aquifer, but the aquitard can be significant in passing water between two aquifers. Third an aquiclude may contain water in great amounts but is entirely incapable of transmitting it. A formation of clay would be a proper example of an aquiclude. Finally, an aquifuge is a subsurafce formation that neither contains water nor transmits it.

The voids or pore spaces within an underground formation and how well

or poorly they are connnected determine the effectiveness of the formation in terms of water storage and tranmission. Only pores that are connected can act as flowing water conduits. The pores can range in size from huge limestone caverns to subcapillaries where the water is held by molecular forces. How water flows within pores will be covered in more detail in the next section.

Subsurface regions can be divided into horizontal zones with respect to how much water each zone contains. The zone of saturation has pore spaces that are completely filled with water. Over the zone of saturation lies the aeration zone where the pores are partially filled with water, air, and water vapor. Further divisions of the aeration zone will help in understanding how pollutants migrate through the different zones.

Precipitation and agricultural irrigation enters the aeration zone through the soil-water zone and migrates down to the vadose region. The capillary fringe is the bottom layer of the aeration zone. The water table boundary or phreatic surface marks the boundary between the zone of saturation and the capillary fringe. The zone of saturation is bounded underneath by an impervious bedrock or clay layer and can be seen in Figure 1-2.

The soil water zone lies directly underneath the ground surface. Plants growing in the soil water zone depend upon water and air, and the moisture profile in this zone depends upon seasons, time of day, humidity, ambient temperature, and the amount of agricultural activity. A shallow water table can also affect the soil water zone.

The vadose zone spans the area between the soil water zone and the

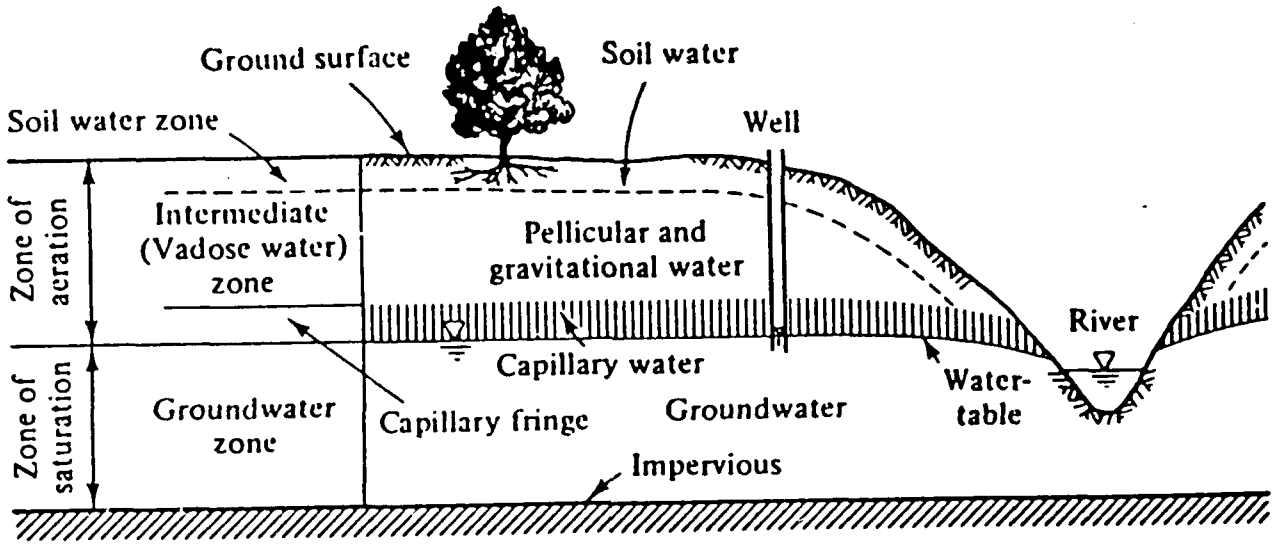


Figure 1-2: Subsurface Horizontal Sections[6]

capillary fringe. The vadose zone's thickness depends upon the height of the water table, and does not exist if the water table extends through the capillary fringe up to the soil water zone. The capillary fringe can border on the soil water zone.

The capillary fringe rises from the phreatic surface up to the capillary limits of the soil. The depth of the capillary fringe is determined by pore size distribution and homogeneity of the soil. In a cohesionless soil, such as sand of gravel, the capillary fringe can be almost non-existant, but in a fine-grained soil, such as clay, the fringe can be 2-3 meters in height.[6] As the height of the capillary fringe increases, moisture content decreases. The largest pores can be saturated near the bottom of the capillary fringe. Moving higher in the capillary fringe, smaller pores are completely filled, and at the highest level only the smallest pores are completley filled with water. This moisture content profile makes for an irregular boundary for the capillary fringe. A smooth average surface is therefore taken as the boundary of the capillary fringe.

Figure 1-2 and the preceding text serve well as a general introduction for the two types of aquifers, unconfined and confined. The zone of saturation shown in Figure 1-2 is an unconfined or phreatic aquifer. Lack of an upper boundary distinguishes this type of aquifer. A confined aquifer is bounded on the top and bottom by an impervious layer. A well penetrating the upper boundary of a confined aquifer will free water to rise to some level above the upper layer. A special type of confined aquifer known as an artesian aquifer will flow freely above the ground surface without being pumped. Both unconfined and artesian aquifers are shown in Figure 1-3.

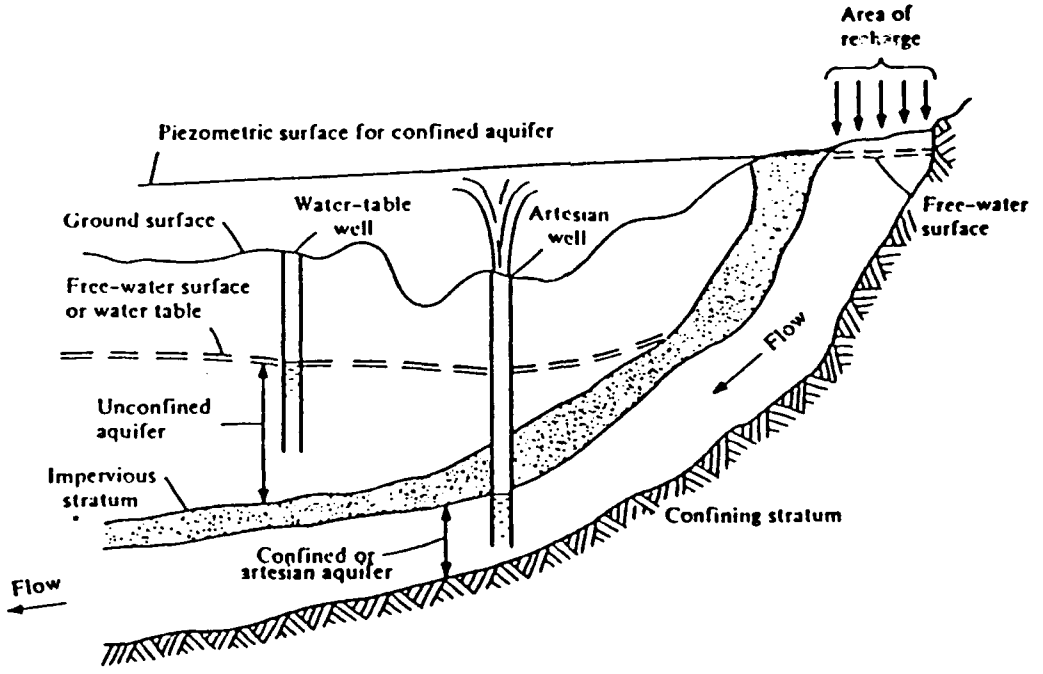


Figure 1-3: Unconfined and Confined Aquifers[5]

Aquifers, both confined and unconfined, can be replenished from infiltration through soil, water from streams and lakes, by transfer of water from other aquifers, and direct injection from a well. Unfortunately

these routes of replenishment offer major pathways for pollutants to contaminate ground water. This contamination can occur by any one or combination of three reasons: accidental pollution, willful misconduct, or negligence. The Congressional Office of Technology Assessment has also grouped 33 types of ground-water contamination sources into six broad categories. These six categories are highlighted in Table 1-2.

Precipitation is the main source of ground water,[26] and infiltration of precipitation is the most common route of ground-water pollution. Rainwater falling to earth migrates downward under the influence of gravity through the layers of the aeration zone. As the water passes through the soil matrix, it dissolves organic and inorganic substances that are present in the soil. The organics and inorganics going into solution form leachate. Similarly water passing down through a poorly managed or abandoned municipal landfill will encounter organic and inorganic substances in greater amounts. This leachate has a much greater potential to damage an aquifer than that produced passing through an undisturbed soil. The leachate continues to move downward until it encounters the saturated zone. As a fuction of time and ground-water movement, the leachate spreads horizontally and vertically possibly contaminating an entire aquifer. Typical levels of organic and inorganic components found in a municipal landfill leachate are provided in Table 1-3.

Ground water normally flows toward an above ground source such as a lake or river, but at certain periods such as a flood, the flow can be reversed. Polluted water from an above ground water source can now enter the ground water. Heavy pumping can also change the normal direction of

Table 1-2: Ground-Water Contamination Sources[e]

Category I - Sources designed to discharge substances

- Subsurface percolation (e.g, septic tanks and cesspools)
- Injection wells
  - Hazardous waste
  - Non-hazardous waste
  - Non-waste (e.g, enhanced recovery, artificial recharge, solution mining and *in-situ* mining)
- Land application
  - Wastewater (e.g, spray irrigation)
  - Wastewater byproducts (e.g, sludge)
  - Hazardous waste
  - Non-hazardous waste

Category II - Sources designed to store, treat, and/or dispose of substances; discharge through unplanned release

- Landfills
  - Industrial hazardous waste
  - Industrial non-hazardous waste
  - Municipal sanitary
- Open dumps including illegal dumping (waste)
- Residential (or local) disposal (waste)
- Surface impoundments
  - Hazardous waste
  - Non-hazardous waste
- Materials stockpiles (non-waste)
- Graveyards
- Animal burial
- Aboveground storage tanks
  - Hazardous waste
  - Non-hazardous waste
  - Non-waste
- Underground storage tanks
  - Hazardous waste
  - Non-hazardous waste
  - Non-waste
- Containers
  - Hazardous waste
  - Non-hazardous waste
  - Non-waste
- Open burning and detonation sites
- Radioactive disposal sites

Category III - Sources designed to retain substances during transport or transmission

- Pipelines
  - Hazardous waste
  - Non-hazardous waste
  - Non-waste
- Materials transport and transfer operations
  - Hazardous waste
  - Non-hazardous waste
  - Non-waste

Category IV - Sources discharging substances as a consequence of other planned activities

- Irrigation practices (e.g, return flow)
- Pesticide application
- Fertilizer application
- Animal feeding operations
- De-icing salts operations
- Urban runoff
- Percolation of atmospheric pollutants
- Mining and mine drainage
  - Surface mine related
  - Underground mine related

Category V - Sources providing a conduit or inducing discharge through altered flow patterns

- Production wells
  - Oil and gas wells
  - Geothermal and heat recovery wells
  - Water supply wells
- Other wells (non-waste)
  - Monitoring wells
  - Exploration wells
- Construction excavation

Category VI - Naturally occuring sources whose discharge is created and/or exacerbated by human activity

- Ground water - surfaces interactions
- Natural leaching
- Salt water intrusion/brackish water upconing or intrusion of other poor quality natural water

flow. The well draw down can become so severe that the surface water has a greater hydraulic gradient and flows back into the aquifer.

Table 1-3: Organic and Inorganic Components Found In A Typical Sanitary Landfill Leachate[7]

Component	Typical Range (mg/L)
K^+	200-1000
Na^+	200-1200
Ca^{++}	100-3000
Mg^+	100-1500
Fe (Total)	500-10,000
Mn^{++}	0.01-100
Cu^+	< 10
Ni^{++}	0.01-1
Zn^{++}	0.1-100
Pb^{++}	< 5
Hg^+	< 0.2
NH_4^+	10-10,000
Cl	300-3000
Alkalinity	10-1000
NO_3	0.1-10
Organic Nitrogen	10-10,000
P as PO_4	1-100
Dissolved organic carbon	200-30,000
COD	1000-90,000
TDS	5,000-40,000
pH	4-8

Transfer of water between aquifers can lead to contamination; an aquifer that has been cantaminated is linked hydraulically with another uncontaminated aquifer. If hydraulic conditions are favorable, i.e., the uncontaminated aquifer is down gradient from the contaminated aquifer, the uncontaminated aquifer will eventually be polluted. Old and improperly abandoned wells are a good conduit for interaquifer transfer. Improperly abandoned wells are also an example of willful misconduct and/or negligence contributing to a ground-water problem.

Direct migration results from leaking underground sources such as

tanks or pipe lines. If tanks or pipe lines lie within the saturated zone, a tremendous opportunity exists for a highly concentrated contaminant plume to evolve. The contaminants are leaking direcly into the aquifer in a pure form.

A source of ground-water contamination can be rainwater infiltration that leaches contaminants from the soil. These contaminants could have come from a poorly managed above-ground tank farm or a leaking above-ground pipeline.

Once the source of contamination has been determined, finding out where the contaminant has been and more importantly where it is going is the next step. Cleaning up contaminated ground water and mitigating its damage requires the ability to plot the present boundaries of the contaminant plume and predict its future movements. Given the nature of the subsurface environment, tracking the movements of ground water can be a difficult proposition, but with mathematical models and techniques, a reasonable guess can be ascertained. The next section is devoted to briefly reviewing the basics of flow through porous media.

Flow Through Porous Media

Two mechanisms are largely responsible for the movement of liquids through a porous media: advection and dispersion. Advection is the bulk transport of fluid, and dispersion is the movement of fluid due to velocity and concentration gradients within a porous matrix.

Advection is bulk fluid movement due to a pressure difference between two points in the porous matrix. This movement can be modeled by Darcy's Law.

$$q = -kA(\delta h/\delta x) \qquad (1\text{-}1)$$

where: q = flow per unit time (L^3/T)
k = coefficient of permeability (L/T)
or hydraulic conductivity
A = cross sectional area normal to flow (L^2)
$\delta h/\delta x$ = headloss per unit length or pressuere drop
across sample

Hydraulic conductivity, k, is a proportionality constant that is a function of both the fluid and the porous media. The hydraulic conductivity is also known as permeability or the coefficient of permeability. This should not be confused with intrinsic permeability. Intrinsic permeability is a characteristic of the porous media alone and is not affected by the properties of the permeant. The relationship between hydraulic conductivity and intrinsic permeability can be seen through two forms of the Darcy equation. The first form is the Darcy equation shown in Equation 1-1. Where in that case k is the hydraulic conductivity. The second form is more fundamental:

$$q = -KgA(\delta h/\delta x)\rho/\mu \qquad (1\text{-}2)$$

where: K = intrinsic permeability (L^2)
g = acceleration due to gravity (L/T^2)
ρ = density of pore fluid (M/L^3)
μ = dynamic viscosity of pore fluid (M/LT)

If equations 1-1 and 1-2 are set equal to each other:

$$k = Kg\rho/\mu \qquad (1\text{-}3)$$

As can be seen, hydraulic conductivity is a function of intrinsic permeability.

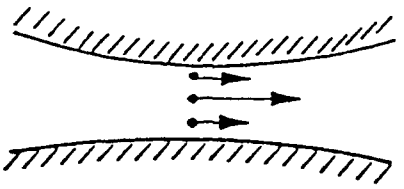
Hydraulic conductivity, k, is normally used to describe the rate at which water flows through a porous media, and intrinsic permeability, K, is used to describe the effects of different pore fluids on hydraulic

conductivity when compared to water. By solving Equation 1-1 for k the velocity of fluid flow can be found and this will provide the amount of time it takes the fluid to go from one point to another.

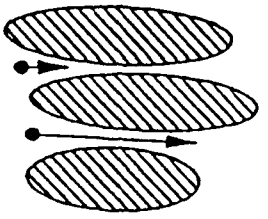
Soil types vary across the land, and quite frequently clay and silts are mixed with the sand and gravel. Clay and silt can also dominate the underground strata. In sand and gravel, advection, the bulk movement of fluid, is the primary mechanism by which pollutants can migrate. Equation 1-1 applies in the case of advective movement. With soils containing or dominated by clays and silts, dispersion becomes an additional mechanism or the only mechanism of fluid and pollutant transport.

Dispersion is divided into two parts: mechanical mixing and molecular diffusion.[6] Mechanical mixing results from velocity gradients within a porous media. These velocity gradients are caused by flow through pores, pore geometry, and fluctuations in streamlines and are shown in Figure 1-4. A situation similar to pipe flow is shown in Figure 1-4a, where the velocity profile shows a greater velocity in the center of the pore opening and lower velocities near the soil grain particles. The pore geometry shown shown in Figure 1-4b depicts a lower velocity between the top and middle soil particles because they are closer than the middle and lower soil particles. Consequently the velocity vector shown at the bottom has a greater value. An arrangement of soil particles that causes streamlines to fluctuate is shown in Figure 1-4c. Any one or any combination of these three pore arrangements can mix a contaminant with pore fluid.

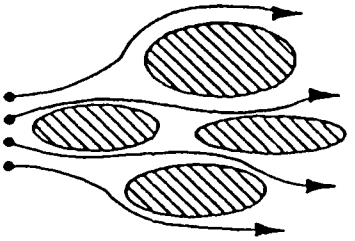
Molecular diffusion results from concentration gradients existing within the fluid itself. Higher concentrations of contaminant will diffuse



a. Flow Thru Pores



b. Pore Geometry



c. Fluctuations in Streamlines

Figure 1-4: Velocity Variations in Porous Media

toward areas of lower concentration. Movement due to diffusion mixes contaminants with the pore fluid.

As mentioned previously, movement of fluid and thus pollutants in soil that is dominated by sands and gravels can be best predicted by the Darcy Equation (Equation 1-1). Fluid movement in soils dominated by clays and silts can be very difficult to predict. One reason for the difficulty of

Physical barrier methods such as interceprtor trenches and wells are important in the containment of contamination as well as a treatment aid. Biological methods have also been used with great success.

Granular Activated Carbon

Granular activated carbon (GAC) has proven to be an excellent adsorber of synthetic organic chemicals because of the amount of surface area available for adsorption. Often the surface area can be as high as 1400 m^2/g.[10] Internal surface areas available for adsorption of an activated carbon sample are shown in Figure 1-5.

The effectiveness of GAC in treating contaminated ground water has been proven many times over.[10,11,12] Several organic compounds such as

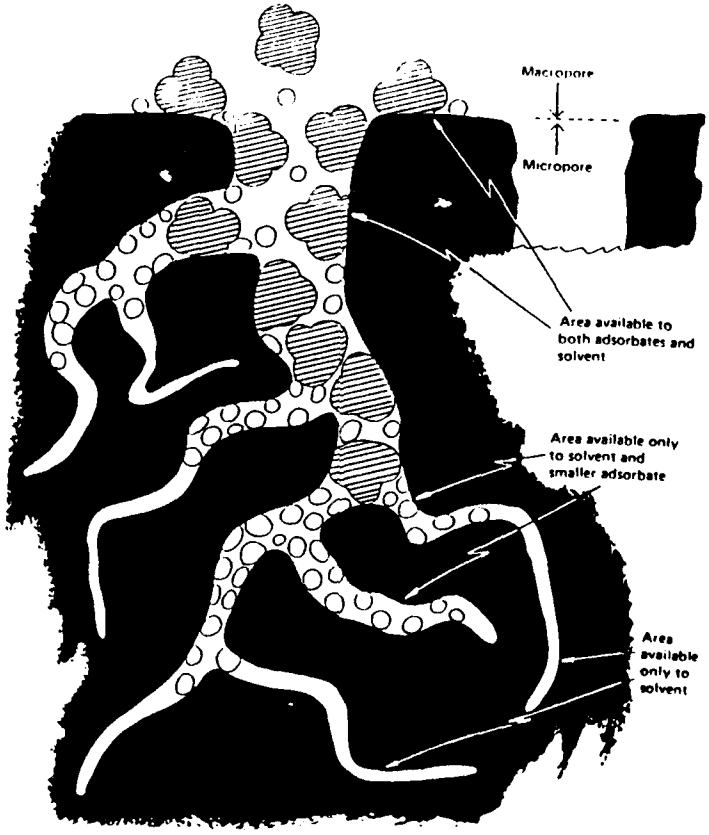


Figure 1-5: GAC Areas Available for Adsorption and Retardation[10]

phenols, chloroform, xylene, their concentrations found in aquifers, and the amount removed by GAC systems are presented in Table 1-4. The GAC systems presented in Table 1-4 had contact times of less than five hours and required no additional treatment.''

Table 1-4: Carbon Adsorption for Organic Contaminants''

System	Contaminants	Influent Conc. (mg/L)	Effluent Conc. (mg/L)	% Removal	Loading (gpm/ft^2)	Contact Time (min)
1.	Phenol	63	<1	>98	1.0	201
	Orthochlorophenol	100	<1	>99	1.0	201
2.	Chloroform	3.4	<1	>71	2.3	262
	Carbon tetrachloride	135	<1	>99	2.3	262
	Tetrachloroethylene	73	<1	>98	2.3	262
3.	Trichloroethylene	3.8	<1	>74	2.4	36

Air Stripping

Air stripping can remove volatile organic compounds from ground water. The process involves placing contaminants in their dissolved liquid state into intimate contact with air so that the contaminants undergo a phase change from liquid to vapor. Spray basins and packed towers are examples of air stripping methods.

Spray basins have been used successfully in the clean up of contaminated sites. With this scheme, a piping grid is laid out on top of a basin. Nozzles spray the contaminated water into the air in the form of a fine mist, and the volatile chemicals are dispersed into the atmoshpere. Spray basins are relatively inexpensive and adapt well to short term clean up situations, but large tracts of land are required. Neighboring land owners also pose a problem. They might not like the fine mist blowing onto their property since it could contain nonvolatile organic chemicals.

Better than spray basins, packed towers are well suited for removing volatile organics down to drinking water standards. Packed towers are compact units which set up with relative ease. The basic concept involves a counter current of air and water; water flows down and air flows up. As they pass, volatile organics undergo the phase change from liquid to vapor and are removed from the water and leave with the air. A schematic of a packed tower system is shown in Figure 1-6. Organic compounds that can be easily removed by the packed tower method are acetone, carbon tetrachloride, tetrachloroethylene, and vinyl chloride.

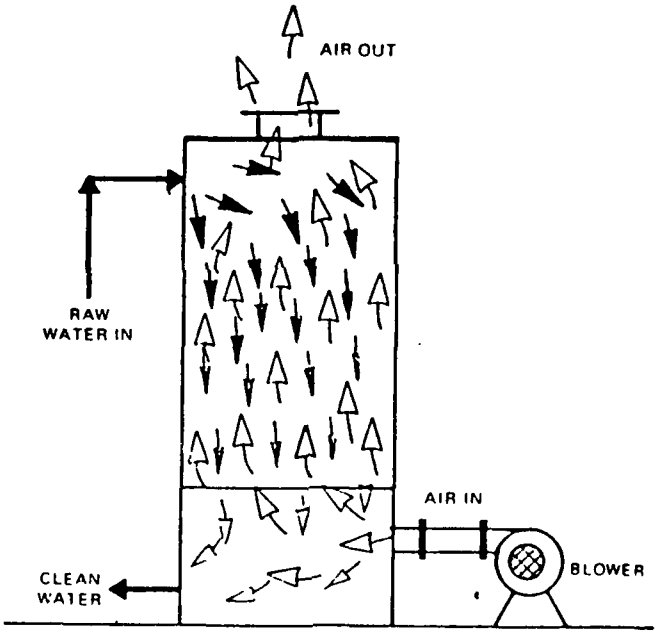


Figure 1-6: Packed Tower Volatile Organic Removal System[10]

Pure Phase Recovery

Pure phase recovery has been used successfully with hydrocarbons.[30] Not only is cleaning ground water a paramount concern, but an economic incentive also exists for removing the hydrocarbon in its unspoiled condition. A hydrocarbon recovered in an unspoiled condition can be used

for its original purpose. These hydrocarbons are generally straight carbon chains, and they are insoluble in water. Gasoline and oil are examples of straight chain hydrocarbons that float on top of an aquifer, and once recovered can be used. Chlorinated hydrocarbons are generally no more soluble than petroleum products, but they are heavier than water. Chlorinated hydrocarbons will sink to the bottom of an aquifer and are more difficult to recover in a pure phase form, but it can be done and they can be used.

A common method for removing gasoline type contamination is by well. A well is bored through the center of the spill as it lays on top of the aquifer. As the well draw down begins to form, gasoline simply moves down gradient into the well and is pumped out to be reclaimed and used. The well method is shown in Figure 1-7.

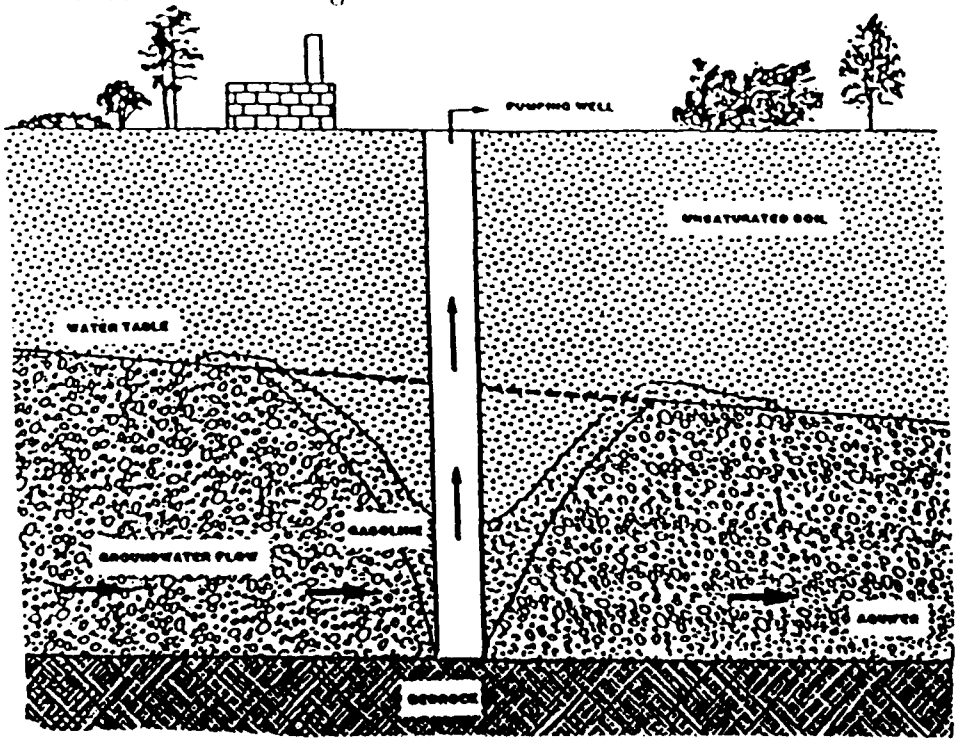


Figure 1-7: Petroleum Product Recovery System[10]

Incineration

Incineration involves elevating the contaminated ground water's temperature to well over 1000°C in the presence of oxygen. If the contamination is greater than 20% organics, then burning will carry on without any additional fuel being added.[14] Ground water is not, however, normally contaminated to this level so additional fuel, such as natural gas, must be added. The addition of fuel and the small number of liscensed incinerators makes incineration a costly alternative. Incineration has been used on a limited basis to burn soil contaminated with toxic chemicals.

Physical Barrier Methods

Physical barrier methods offer a positive approach to the containment, treatment, and ultimate disposal of a contaminated ground water plume. They are also a necessary ingredient to successful management of a waste treatment or disposal sight.

Interceptor trenches have proven to be an effective ground-water control method at waste management sites.[15] Interceptor trenches, in their simplest form, are constructed by excavating a continuos trench in the earth and replacing the excavated spoil with a highly permeable material such as gravel to permit drainage. The basic design is shown in Figure 1-8. A more sophisticated version has a perforated drainage tube placed in the bottom of the trench. This tube is attached to a sump where contaminated water is collected and treated or disposed. The centerline of the trench is the line of lowest pressure in the ground water; all water within the influence of the trench must flow towards it. Since pressure

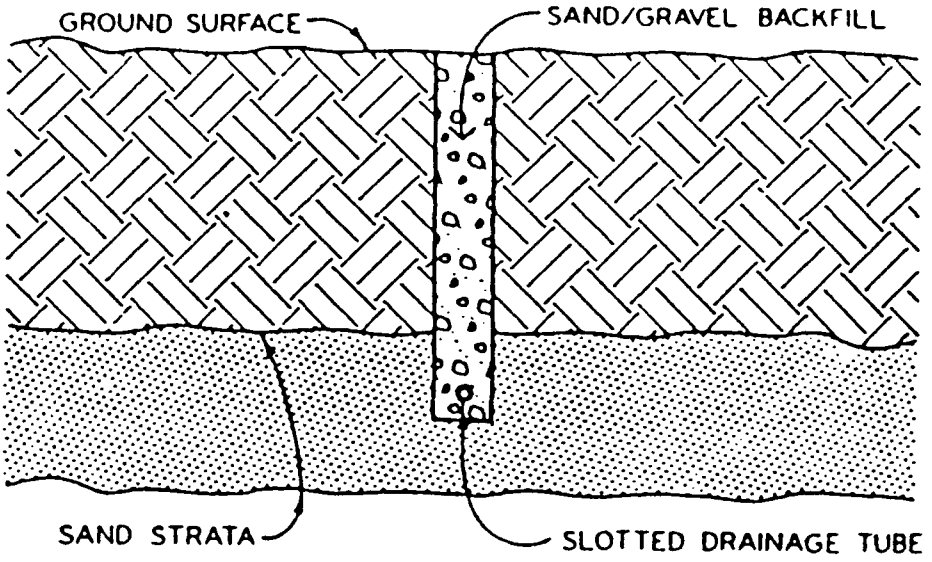


Figure 1-8: Cross Section Of A Basic Interceptor Trench[15]

is greater on either side of the trench, flow across or away from the trench is impossible. Another physical barrier method that can control ground-water movement is a grid of pumping and/or injection wells.

Well systems for ground-water control are based on artificially changing underground flow patterns with pumping or injection wells. Wells directly affect the movement of ground water and indirectly affect the movement of the contaminants. This has the effect of pushing or pulling the plume in a controlled and specified direction. Three methods are generally used to manage the plume in the above mentioned fashion. The first two involve pumping wells at deep and shallow levels. The third involves injection wells and is often called a pressure ridge system.

Above Ground Biological Treatment

Although the use of biological treatment for domestic and industrial wastewaters is a common practice for many municipalities across the United States, the use of biological treatment methods must be more carefully

considered for contaminated ground water. A major obstacle to seeing a proliferation of activated sludge systems for ground-water cleanup is that they must be run 24 hours a day. Activated sludge systems cannot be turned off because microorganisms that degrade contaminants must be given a constant source of substrate, nutrients, and oxygen or they will begin to die. Another short coming is that most biological systems such as activated sludge are not designed for influent concentrations lower than 50-75 mg/L. Typical ground-water concentrations are in the low µg/L range. But for a comparison of the potential of biosystems, the fate of 23 priority pollutants in a conventional activated sludge system as compared to two alternative treatment methods previously discussed, GAC and air stripping, is shown in Table 1-5. The majority of these priority pollutants are degraded significantly by biodegradation.

Biological systems are generally placed into two categories, suspended growth and fixed film. Activated sludge is the suspended growth system highlighted in Table 1-5. Fixed film systems include rotating biological contactors and packed towers. With a suspended growth system microbes that degrade contaminants as part of their normal metabolism float freely within a polluted aqueous medium. Pollutants act as a carbon source to provide energy for cell maintenance and growth. With a fixed film system, microbes attach themselves to a medium such as redwood or plastic, and the polluted water flows over the microbes. Organic contaminants diffuse into microbes where they are used as a carbon source for maintenance and growth.

Conventional application of biological systems, both suspended andfixed film, for the clean-up of contaminated ground water involves the

pumping of ground water out of the ground and through a treatment plant.

Table 1-5: Comparative Treatment Methods for Priority Pollutants[1,2]

Compound	Percent Treatment Achieved		
	Stripping	Sorption	Biological
Nitrogen Compounds			
Acrylonitrile			99.9
Phenols			
Phenol			99.9
2,4-DNP			99.3
2,4-DCP			95.2
PCP		0.58	97.3
Aromatics			
1,2-DCB	21.7		78.2
Nitrobenzene			97.8
Benzene	2.0		97.9
Toluene	5.1	0.02	94.9
Ethylbenzene	5.2	0.19	94.6
Halogenated Hydrocarbons			
Methylene Chloride	8.0		91.7
1,2-DCE	99.5	0.50	
1,1,1-TCE	100.0		
1,1,2,2-TCE	93.5		
1,2-DCP	99.9		
TCE	65.1	0.83	33.8
Chloroform	19.0	1.19	78.7
Carbon Tetrachloride	33.0	1.38	64.9
Oxygenated Compounds			
Acrolein			99.9
Polynuclear Aromatics			
Phenanthrene			98.2
Napthalene			98.6
Phthalates			
Bis(2-Ethylhexyl)			76.9

The clean water must be injected back into the ground or discharged into a receiving stream. The unconventional application of biological systems is to allow the contaminated ground water to be treated *in situ*.

In Situ Biological Reclamation

In situ reclamation is the restoring of ground water to an environmentally acceptable condition by rendering contaminants harmless

while not removing them from the aquifer. In general there are two methods[39] to achieve this result. The first is to add acclimated microbes and nutrients to the polluted aquifer. Acclimated microbes are obtained by enriching a seed culture or genetic manipulation of a strain of bacteria, the so called "designer bugs". Acclimated microbes can be pumped into the contaminated aquifer by injection wells. The second method is to add dissolved nutrients and oxygen in order to enhance natural subsurface biological activity. Nutrients and oxygen can be pumped down into the aquifer with injection wells and allowed to mix with the contaminated ground water.

Microorganisms can become acclimated to a particular pollutant by repeated exposure to that substance. Felsot, *et al.*,[40] reported a strain of bacteria became so used to the pesticide carbofuran that it no longer was effective against corn rootworms. Spain and Van Veld[41] suggested that small amounts of the pollutant might be added to the region around a contaminant plume to insure a rapid microbial response.

Genetic manipulation of a bacterial species can also enhance the species ability to degrade certain pollutants. One method has been to augment the species' DNA with extra chromosomes called plasmids.[42] The plasmids alter the basic makeup of the cell enough to allow the bacteria to now degrade more compounds. Kellogg, *et al.*,[43] developed a strain of *Pseudomonas cepacia* whose sole food source was 2,4,5-trichlorophenoxyacetic acid, better known as the pesticide 2,4,5-T.

Raymond[39] and his people at Suntech pioneered work in "bioreclamation". Their method supplied dissolved oxygen and nutrients to

the indigenous microbial population in order to enhance the subsurface biological activity. Depending upon the size of the contaminated area, a tremendous mount of nutrients may be required. Minugh, *et al.*,[43] reported the use of 16.65 tons of nutrients, and another site required the addition of 87 tons[44] of food grade quality chemicals. The oxygen can be introduced by air diffusers in a well, air diffusers along an injection trench, or through the addition of hydrogen peroxide.

An exhaustive combination of lab and field studies are required before a version of the bioreclamation technique or genetically altered organisms can be introduced into the natural environment.

Experimental and Field Study Basis for *In Situ* Treatment

Treating contaminated ground water without removing it from the ground is now under intensive study. *In situ* biological treatment of ground water contaminated by organic chemicals is indicated as a viable and cost effective alternative. Many contaminants in solution in ground water as well as vapors in the unsaturated zone can be completely degraded or transformed into new compounds by naturally occuring indigenous microbial populations.[45]

Because of the relatively young age of this field of study, no set methodolgy has been developed to determine if natural biorestoration is occuring, how far it is along, what products are being produced as a result of biorestoration, or what the long term effects of biorestoration will be. But in recent years, much has been discovered about environmental factors that affect the underground microorganism's ability to degrade organic contaminants. Environmental factors that affect biorestoration are

availability of nutrients, pH, dissolved oxygen content, reduction-oxidation potential, temperature, soil moisture content, salinity, and pollutant concentration.[40] Laboratory work has been done to establish the fact that underground microbial life can degrade synthetic organic contamination. Work has also moved from the lab into the full scale field tests.

Only within the last 10 to 15 years[31,32] has the literature recognized the existance of microfauna and flora beneath the surface of the ground. Before this the prevailing thinking had been conditions only a few centimeters below the ground's surface were nearly devoid of life.[33] The idea of sterility could have propagated by the work of Waksman[17] in 1916. Waksman[17] concluded there was a rapid decline in microbial populations as soil depth increased. However Ghiorse and Balkwill[18] concluded in 1983 that as many as one million microbes per gram of soil could exist well below the surface. Harvey[34] demonstrated in a Cape Cod, Massachusetts aquifer that between 10 and 100 microorganisms were common on each soil particle surface. He also showed that with 95% of the microorganisms attached to the soil particles an *in situ* treatment system would be a fixed film system.

Laboratory Studies

The next logical step after concluding microbial life does exist underground was to determine if this life could degrade synthetic organic chemicals. Bouwer and McCarty[45] in laboratory experiments concluded microorganisms in a methanogenic environment could degrade SOCs.

Bouwer and McCarty[45] used an upflow reactor containing 3-mm glass

beads to demonstrate that a greater than 90% reduction in 1- and 2-carbon halogenated aliphatic compounds could take place in two days. The concentrations of compounds were trace amounts (μg/L) and were introduced into the reactor with an acetate primary substrate. Compounds used in their work were chloroform (CF), carbon tetrachloride (CT), 1,1,1-trichloroethane (1,1,1-TCE), trichloroethylene (TCE), 1,1,2,2-tetrachloroethane (1,1,2,2-TECE), tetrachloroethylene (TECE), 1,2-dibromoethane (1,2-DBE), dibromochloromethane (DBCM), bromodichloromethane (BDCM), bromoform (BF), and 1,2-dichloroethane (1,2-DCE).

Bower and McCarty [45] placed two [2.5-cm (ID) by 22-cm] glass columns filled with 3-mm glass beads in series. The 3-mm glass beads simulated the porous matrix found in the underground environment. Figure 1-9 is a

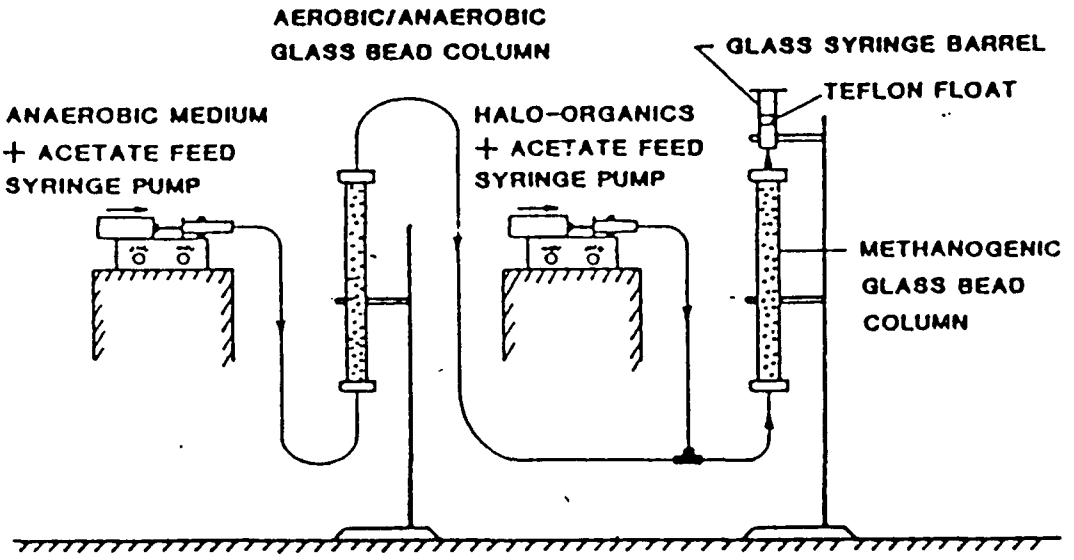


Figure 1-9: Bouwer and McCarty's Laboratory Scale Columns and Continuous Flow System[45]

schematic of the experimental apparatus. The first column received the primary substrate, sodium acetate, at a concentration of 1000 mg/L and was microbially seeded with primary sewage effluent. The effluent out of the first column was the anoxic influent for the second column. Halogenated aliphatic compounds were pumped into the second column as a secondary substrate at a concentration of 160 μg/L. Microbial seed for the second column was taken from a laboratory scale methanogenic anaerobic filter treating rum distillery wastewater. The liquid detention time in the second column was two days. Having the two columns in series assured anaerobic conditions were maintained.[45] Bouwer and Cobb[19] in similar experiments three years later using upflow reactors with 3-mm glass beads experimentally verified that heterotrophic oxidation, denitrification, and sulfate respiration could also take place.

Running concurrently with the continuous flow column experiments Bouwer and McCarty[45] also conducted methanogenic batch experiments which aided in determining the biodegradibility of the halogenated aliphatic compounds. The results of one of the batch experiments are shown in Table 1-6.

The upflow column experiments, like the batch experiments, resulted in a significant percentage removal of the halogenated aliphatic compounds. The results of Bouwer and McCarty's[45] upflow column experiments including all compounds are shown in Table 1-7. It is significant to note that 1,1,2-TCE was not added in the influent but appeared in the effluent after the addition of 1,1,2,2-TECE, and TCE (also not in the influent) appeared in the effluent after TECE was added.

Using an even larger upflow column (20 cm (ID) by 200 cm) with 6-cm

Table 1-6: Degradation of Halogenated Aliphatics in Methanogenic Batch Experiment[45]

Compound	Time (days)	Concentration[a] (µg/L)	
		Sterile controls	Seeded cultures
CT	0	149 ± 15	ND[b]
	16	ND	<0.1
	54	145 ± 15	<0.1
1,1,1-TCE	0	229 ± 23	ND
	16	ND	35 ± 4
	54	227 ± 23	0.3 ± 0.3
TCE	0	178 ± 18	ND
	16	ND	171 ± 17
	57	180 ± 18	107 ± 11
TECE	0	152 ± 15	ND
	16	ND	160 ± 16
	57	162 ± 16	<0.1

a-One standard deviation of mean values is given. b-ND: Not Determined

diameter quartzite rocks forming the porous matrix, Vogel and McCarty[46] demonstrated that tetrachloroethylene (PCE) was biologically transformed to TCE by reductive dehalogenation. This confirmed Bouwer and McCarty's[45] work that showed TCE as an effluent product even though it was not in the influent (see Table 1-7 notes c and e).

Vogel and McCarty's[46] work helped define the biotransformation stages of PCE by demonstrating the presence of intermediate products, dichlorethylene (DCE) and vinyl chloride (VC) as well as TCE. Potential exists for the complete mineralization of PCE to CO_2 under anaerobic conditions in soil and aquifer systems.[46] The concentrations of PCE and its intermediates at the 10 and 22 day points are shown in Figure 1-10. Samples were taken at ports 0-cm, 10-cm, 50-cm, 110-cm, and 180-cm above

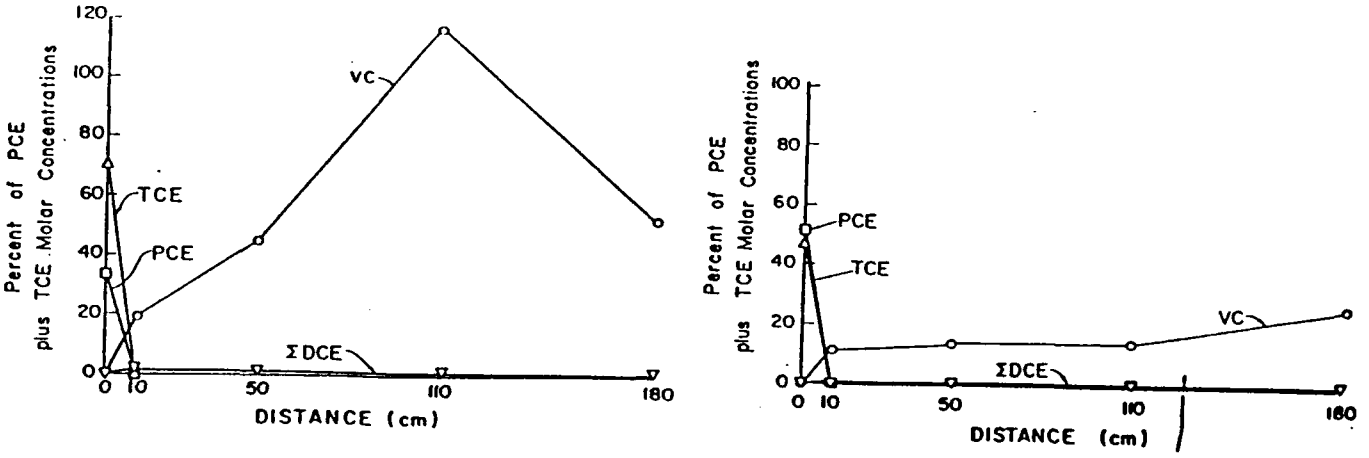
Table 1-7: Average Halogenated Aliphatic Concentrations In Methanogenic Column Influent and Effluent After Acclimation[45]

Compound	Acclimation Period (wk)	Column Influent[a] (µg/L)	Column Effluent[a] (µg/L)	% Steady-State Removal
CF	10	33 ± 7	1.2 ± 0.6	96 ± 2
BDCM	0	30 ± 4	<0.1	>99
DBCM	0	34 ± 5	<0.1	>99
BF	0	34 ± 4	<0.1	>99
CT[b]	0	17 ± 1	<0.1	>99
1,2-DCE[b]	>16	22 ± 3	24 ± 3	-1 ± 20
1,1,1-TCE	10	25 ± 3	0.55 ± 0.3	98 ± 1
1,1,2-TCE[c]	--[d]	0	2.5 ± 1.1	--
TCE[c]	--	0	1.2 ± 0.6	--
1,1,2,2-TECE	0	27 ± 1	0.9 ± 0.7	97 ± 3
TECE	10	18 ± 3	2.6 ± 1.3	86 ± 7
Acetate (12 mo)	0	600 ± 60 mg/L	42 ± 6 mg/L	93 ± 2
Acetate (13 mo)[f]	0	100 ± 5 mg/L	37 ± 3 mg/L	63 ± 4

a One standard deviation of the mean values (24 samples)
b Compound added after 15 months of operation
c Compound detected in effluent after the addition of 1,1,2,2-TECE
d --, None
e Compound detected in effluent after 10 weeks of operation
f Acetate feed concentration was reduced after 12 months to 100 mg/L

the influent point.

Parsons, *et al.*,[47] performing work similar to Vogel and McCarty[46] also demonstrated the presence of intermediate products during biotransformation in a reducing environment of the organic solvents tetrachloroethene (PCE) and trichloroethene (TCE) . However, Parsons, *et al.*,[47] used static microcosms containing ground-water sediments thus closer approximating the actual behavior of organic solvents in an underground environment. The ground-water sediments consisted of muck, decayed vegetation, and marl, the carbonaceous precipitate of algal growth. The muck or marl was added along with a spike of organic solvent to 50-ml



10-Day Point 22-Day Point

Figure 1-10: Profiles of PCE and Its Intermediates At Two Points In Time[46]

septum bottles.

PCE was transformed into TCE and *cis*- and *trans*-1,2-dichlorethene. TCE was transformed into *cis*- and *trans*-1,2-dichloroethene and chloroethene (CE). CE was found in 3 of 24 microcosms, but the appearance of CE was random and thought to be transient.[47] Results of their work are shown in Table 1-8 and are similar to the results of Vogel and McCarty.[46]

Table 1-8: Transformation of Tetra- and Trichloroethene In Ground-Water Sediment Microcosms[47]

	Products Formed (µg/L)					
	Spike: PCE[a]			Spike: TCE[b]		
Time (weeks)	TCE	Cis	Trans	Cis	Trans	CE
0	ND[c]	ND	ND	ND	ND	ND
2	510	300	Trace	38	85	ND
8	20	80	Trace	30	Trace	57
12	8	35	ND	Trace	ND	ND
16	Trace	ND	ND	1,200	ND	ND

a PCE spike concentration 4.2 mg/L
b TCE spike concentration 3.7 mg/L
c ND-Not Detected

It was highlighted in Parsons', *et al.*,[47] work that all microcosms that exhibited transformation of the organic solvents had viable microorganism cultures growing in them. Where no microorganism cultures could be produced, no transformation of the solvents took place. No attempt was made to identify the microorganisms, but more information was gathered on the fate of PCE in a ground-water environment.

Wilson, *et al.*,[48] added to the information provided by Vogel and McCarty[46] and Parsons, *et al.*,[47] concerning the fate of chlorinated aliphatics. Wilson, *et al.*,[48] showed that through reductive dehalogenation PCE went to TCE; TCE went to DCE, and DCE went to VC. No mineralization of VC to CO_2 was reported. They also provided valuable information concerning aromatic compounds such as benzene, toluene, and *o*-xylene. These three compounds typically are found in ground water as a result of gasoline tank leaks.

Benzene, toluene, and the isomers of xylene, the so called "BTX" fractions of gasoline, were degraded in laboratory microcosms containing methanogenic aquifer material from an area adjacent to a central Oklahoma landfill. The results from this portion of their experiment are shown in Table 1-9. Benzene, toluene, ethylbenzene, and *o*-xylene were added together in the concentrations shown in "Week 0". The "Living" and "Autoclaved" samples contained ground water taken from the site where the aquifer material was taken, and the "Autoclaved H_2O" samples had water that had been treated with a reverse osmosis process. The last four samples in the "Autoclaved H_2O" were not analyzed.

Major's, *et al.*,[49] work also centered on studying the fate of the BTX

Table 1-9: Disappearance of Aromatics in Methanogenic Aquifer Material[48]

Treatment	µg/L of Pore Water					
	Week 0	Week 6	Week 12	Week 20	Week 40	Week 120
			Living			
Benzene	613	438	499	491	174	1.6
Toluene	547	73	115	92	2.9	1.5
Ethylbenzene	269	218	224	238	69	1.3
o-xylene	257	215	192	204	56	1.2
			Autoclaved			
Benzene	613	770	645	796	634	426
Toluene	547	692	588	672	489	368
Ethylbenzene	269	297	277	264	222	197
o-xylene	257	310	278	246	230	171
			Autoclaved H_2O			
Benzene	613	699	630	776	530	--
Toluene	547	747	656	753	460	--
Ethylbenzene	269	327	313	328	218	--
o-xylene	257	326	330	314	221	--

fractions, but they used nitrate and oxygen as electron receptors. They showed a much faster degradation of BTX in the presence of nitrates and oxygen. Their microcosms also contained genuine aquifer material and ground water from a Canadian site that had been previously exposed to BTX. This previous exposure to BTX provided acclimated microorganisms. Sterile controls were used as a comparison. The initial concentration of all compounds was 3 mg/L, and two isomers of xylene were used, *o*- and *m*-. The percentages remaining of each compound after 62 days incubation is shown in Table 1-10.

Further laboratory studies have been conducted using microcosms also with genuine aquifer material. Suflita and Miller[74] performed such work with chlorophenolic compounds. They performed two studies under aerobic and anaerobic conditions. Microoganisms for the aerobic study were

Table 1-10: Percentage of BTX Remaining After 62-Day Incubation Period With Nitrate Under Anaerobic and Aerobic Conditions[49]

	Condition				
Compound	Sterile	Nitrate	Anaerobic	Nitrate + Oxygen	Oxygen
Benzene	79	5	66	0	1
Toluene	86	2	65	0	0
o-xylene	80	15	73	19	15
m-xylene	80	12	59	8	11

obtained from a designated clean aquifer near Pickett, Oklahoma, and the microorganisms for the anaerobic study were obtained from two sites that border the municipal landfill in Norman, Oklahoma. Chlorinated phenolic compounds appear in the environment as a result of their use as disinfectants in hospitals and in the pesticide industry.[14]

Suflita and Miller[24] established chlorophenolic compounds could be degraded in a methanogenic aquifer by replacing the chloride ion with hydrogen ions, as confirmed with mass spectrometry. Results from an anoxic nonmethanogenic aquifer showed no degradation of chlorinated phenols while an aerobic aquifer material showed degradation. However, the pathways for this degradation were not identified. The chlorinated phenolic compounds used and results of the experiments are shown in Table 1-11. As can be seen, phenol was also degraded in all ground-water microcosms.

Field Studies

In the Upper Rhine Graben of West Germany, approximately 20 to 30 tons[21] of spilled hydrocarbons were degraded with *in situ* microbial populations. The site was a closed refinery where for years hydrocarbons, both aliphatic and ring compounds, had leaked into the aquifer. This site cleanup was a cooperative effort among an engineering firm, two academic

Table 1-11: Chlorinated Phenolic Compounds and Results[24]

Compound	Anaerobic		Aerobic	Bio-Evidence	
	Nonmethanogenic	Methanogenic		Aerobic	Anaerobic
Phenol	+	+	+	1	1
2-Chlorophenol	0	+	+	1	1,3
3-Chlorophenol	0	+	ND	--	1,3
4-Chlorophenol	0	+	ND	--	1,2,3
2,4-Dichlorophenol	0	+	+	1	1,2,3
2,5-Dichlorophenol	0	+	ND	--	1,2,3
2,4,6-Trichlorphenol	ND	ND	+	1	--

+ - degraded
0 - not degraded
ND - not determined

1 - substrate disappearance
2 - intermediate metabolite formation
3 - gaseous end product formation

institutions, and the West German government. Three years of pumping preceeded the actual *in situ* cleanup.

After three years of pumping, the contamination consisted of a residual saturation left in pore volumes. Soil samples showed oil in 1% of the pore volumes. Figure 1-11 is a plan view of the contaminated site with the estimated extent of contamination. The plan for cleaning the aquifer had three phases. First, an artificial hydraulic flow scheme was established with pumping and injection wells. Second, an above ground treatment system that could remove volatile fractions from the contaminated ground water was established. The above ground treatment system consisted of three pumping wells that sent contaminated water to be air stripped by spraying the water into ponds. The water was then filtered and pumped back into the ground. The above ground treatment facilities are shown in Figure 1-12. The third part involved putting nitrates and nutrients into water pumped back into the ground. Nitrates acted as an electron acceptor, and nutrients provided essential elements for microbial life underground.

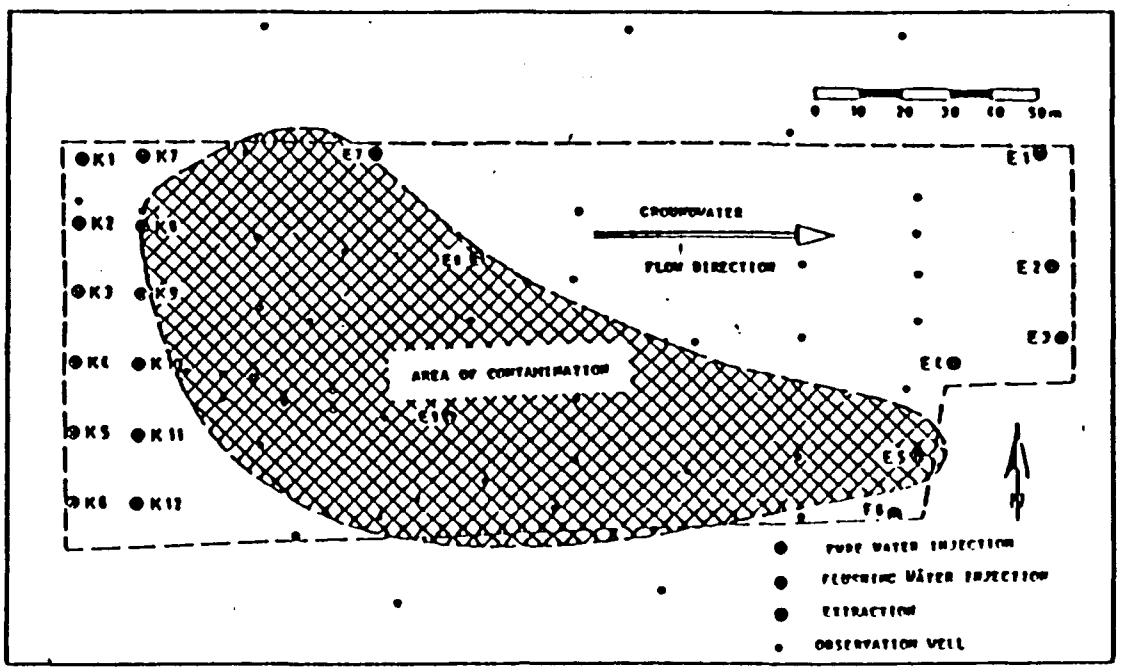


Figure 1-11: Contaminated Site With Well Locations and Extent of Contamination In Upper Rhine Graben, West Germany[21]

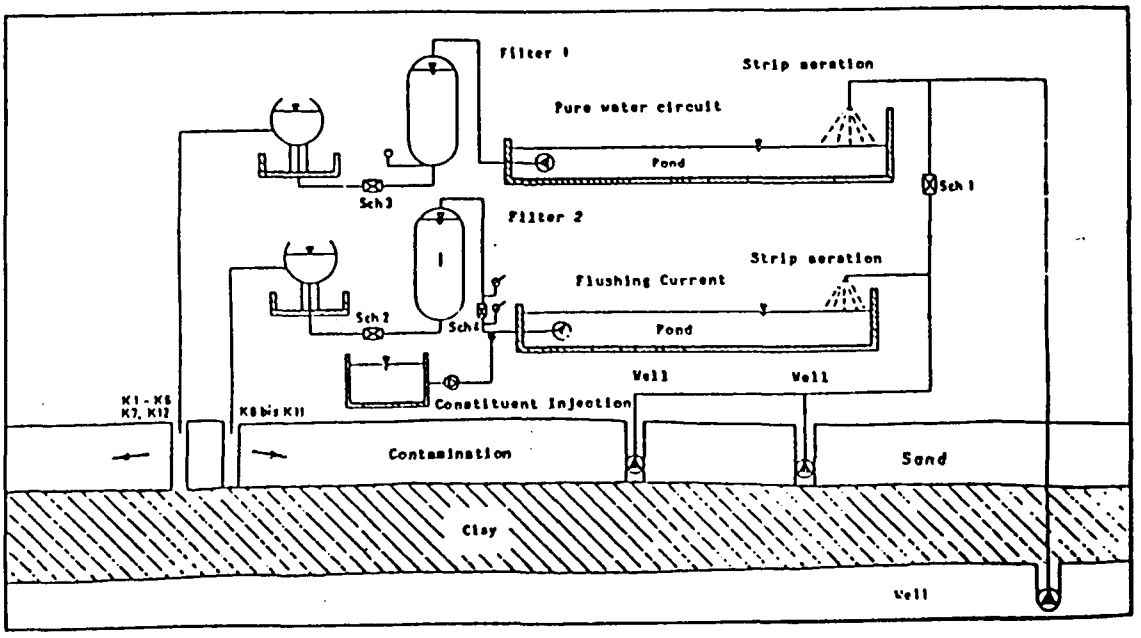


Figure 1-12: Above Ground Treatment Facilities[21]

After a year of operation a reduction in both the aliphatic and ring compound concentrations was noticed. The results of the *in situ* effort are shown in Figures 1-13 and 1-14. A reduction in the aliphatic concentration is shown in Figure 1-13, and a reduction in the ring compounds', benzene, toluene, and xylene, councentration is shown in Figure 1-14. Samples for these data were taken from well E-7 as shown in Figure 1-11. The reduction in aliphatic concentrations as well as ring compound concentrations after the introduction of nitrates and nutrients provided a strong indication that biological life was stimulated. The pollutants were degraded as a result of biostimulation.

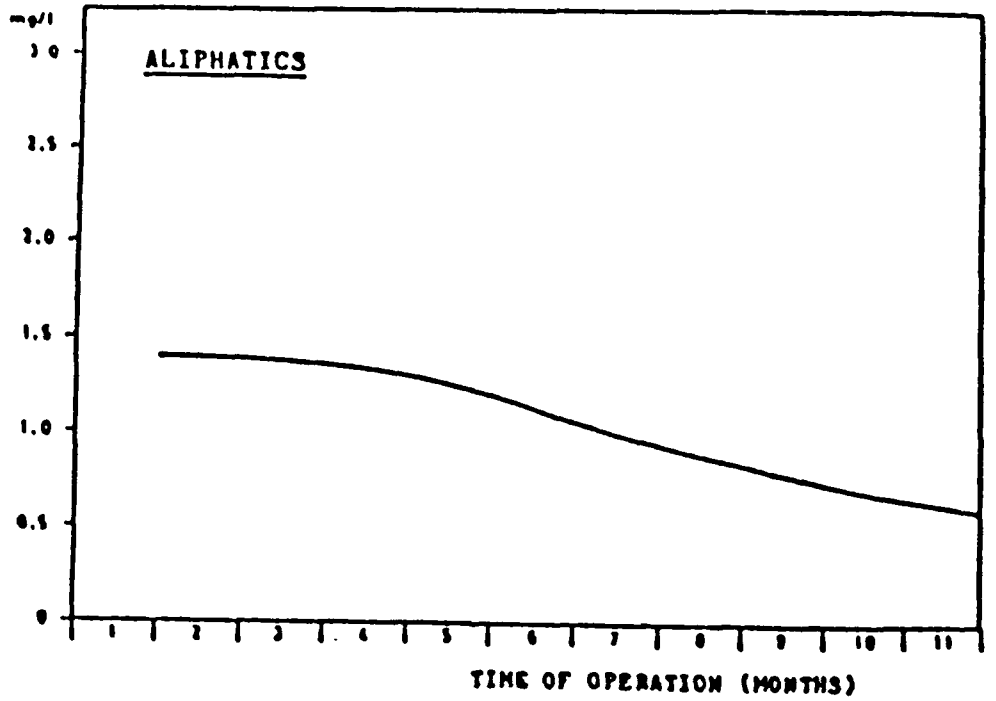


Figure 1-13: Reduction in Aliphatic Concentration in Upper Rhine Graben Project[21]

The West German site was termed successful in the sense that contaminant concentrations were lowered to acceptable levels that were not

harmful to human health and did not violate environmental laws.[21] But a general scheme for solving all similar ground-water problems should not be derived from this experience. Every situation must be evaluated on its own merits with possible modifications to any or all of the steps taken in this German effort.

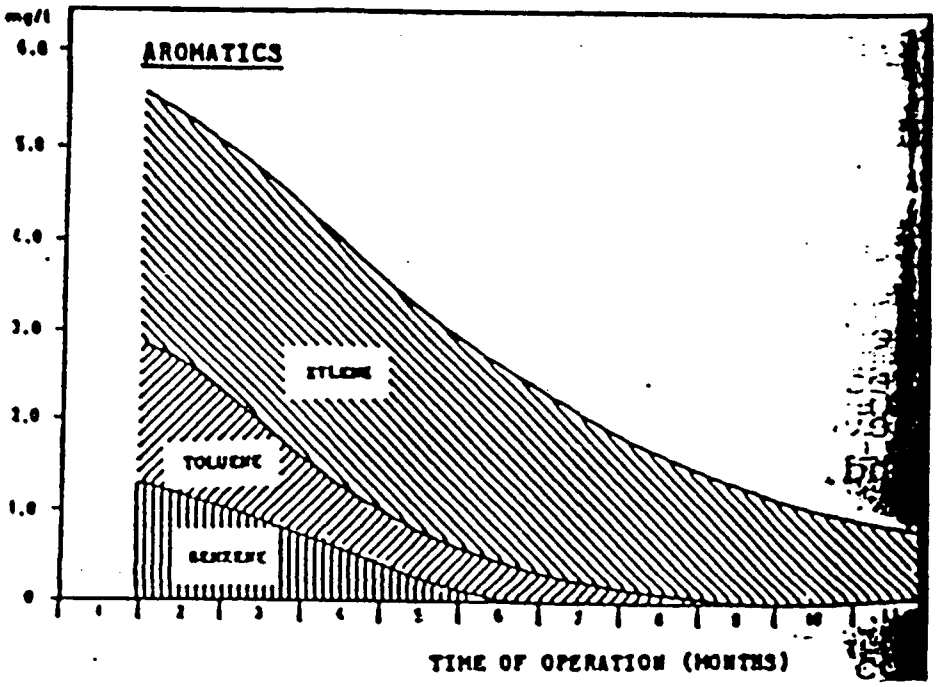


Figure 1-14: Reduction In Ring Compound Concentrations in Upper Rhine Graben Project[21]

Another field scale *in situ* test is currently underway at Kelly Air Force Base in San Antonio, Texas. The site chosen for the field scale test was identified during the base's Installation Restoration Program (IRP) Phase I project. The IRP project discovered that from 1940 to 1955 the site was used to dispose of choromium electroplating wastes. From the early 1960's to approximately 1966, it was used as a chemical evaporation pit for waste solvents and other organic chemicals. After 1966 the site was covered with a thin layer of gravel and a layer of asphalt. A cross

section of the site, as revealed by soil borings, is shown in Figure 1-15. The water table was located 7.6 meters below the surface and rested on a

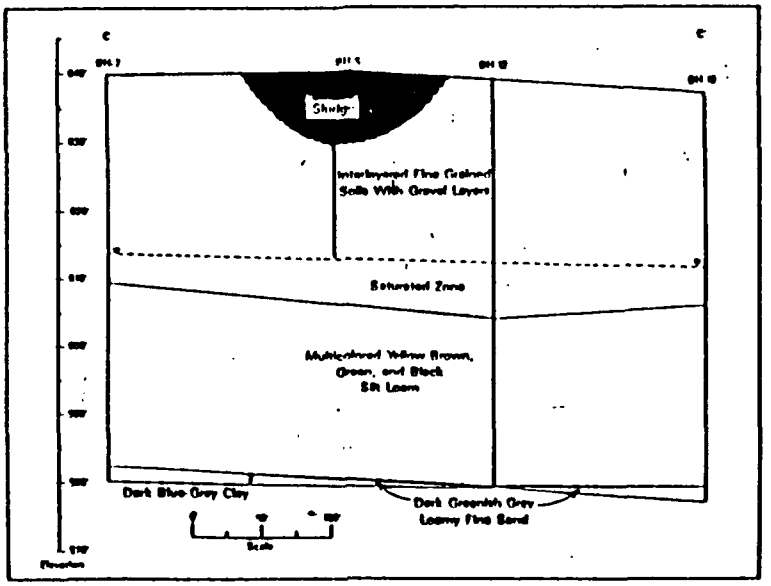


Figure 1-15: Cross Section of Kelly AFB Contaminated Site[22]

silty loam type of soil.

Laboratory soil-water microcosms (240 mL) established the treatability of organic chemicals in the contaminated site. Two kinds of electron acceptors, oxygen and hydrogen peroxide, were used during these tests with results shown in Figure 1-16. The three compounds shown in Figure 1-16, 1,1-dichloroethane, chlorobenzene, and 1,1-dichloroethylene, were representative of the mixture of organic chemicals placed in the evaporation pit.

Aerobic degradation was chosen because more compounds could be degraded and a direct transfer of technology could be used from gasoline spills.[23] From laboratory work that was performed, project engineers decided the most efficient means of getting oxygen into the underground environment was to use hydrogen peroxide.

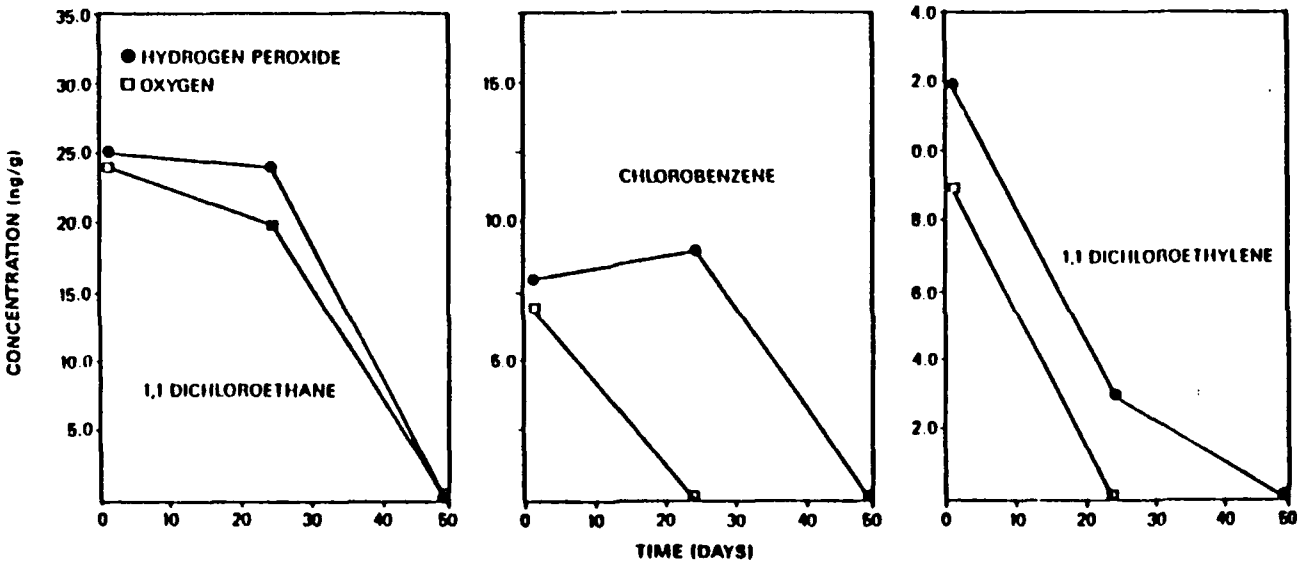


Figure 1-16: Concentration Changes In Aerobic Microcosms from Kelly AFB Field Study[23]

The project engineers realized that hydrogen peroxide had its problems; metals deposited by the chrome plating operation could be mobilized and contaminate the ground water. The oxygen content in high concentrations of hydrogen peroxide, if released too quickly, could surpass the dissolved oxygen saturation point of the ground water forming gas bubbles that would clog the aquifer. The hydrogen peroxide/nutrient feed could escape to a nearby stream and cause an algal bloom because of the nutrients. The hydrogn peroxide could simply decompose into water and oxygen.

The microcosms showed promising results with regard to biodegradation, but hydraulic conductivity tests were also run, and their results were not promising. Soil samples were taken from the contaminated site and tested for hydraulic conductivity using triaxial permeameters. These samples were run with a hydrogen peroxide/nutrient feed water. Results of these tests

are presented in Figure 1 17. As can be seen in Figure 1-17, the ability of the samples to transmit pore fluid in a timely manner quickly went down. A hydraulic conductivity of less than 1 x 10 $^{-4}$cm/s did not allow the proper flow of water, and the necessary transfer of nutrients and oxidant was stopped.

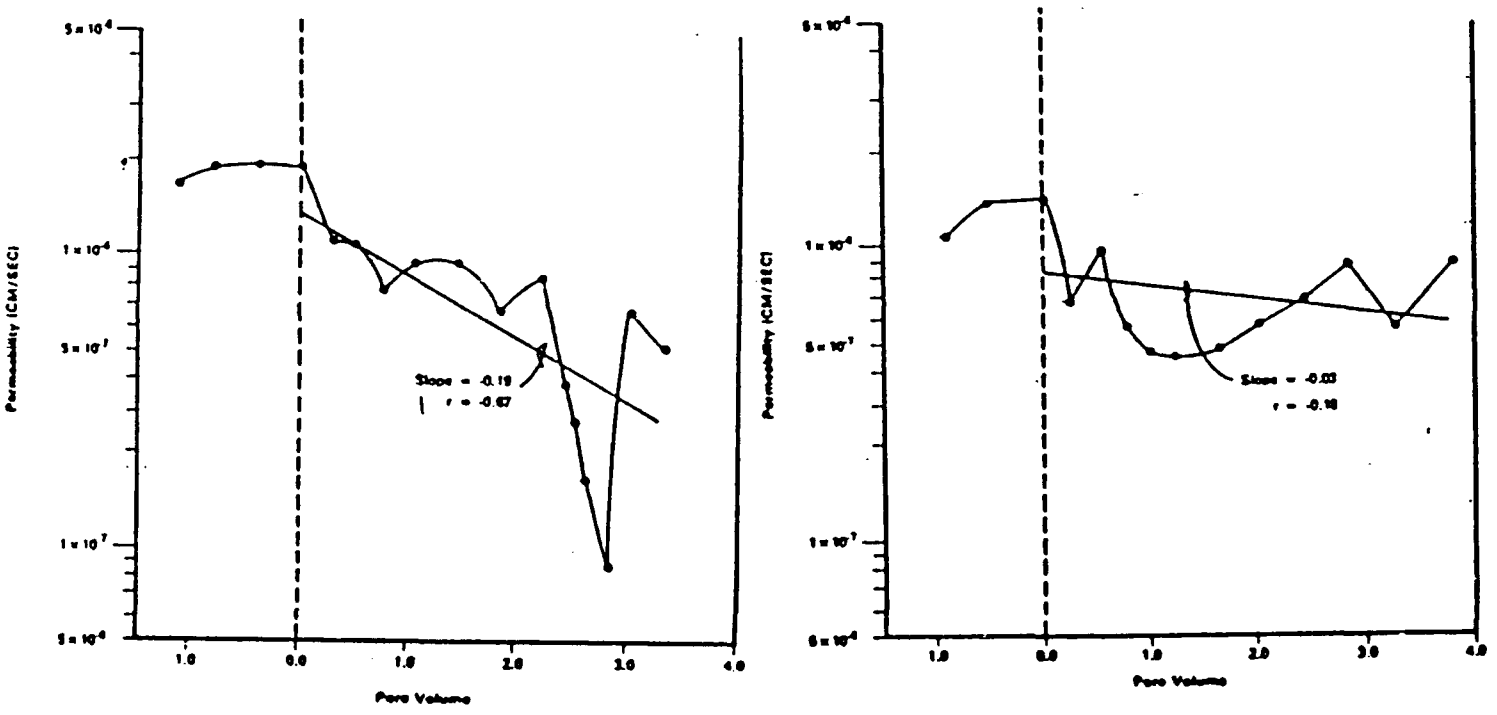


Figure 1-17: Hydraulic Conductivity From Field Samples at Kelly AFB[22]

Based on the Air Force's laboratory and field data, they have opted to continue *in situ* remediation efforts and will work problems out as they are identified. The project engineers also recommended continued lab studies with *in situ* anaerobic degradation.

Most recently Piotrowski[50] working with a team of engineers from Woodward-Clyde Consultants conducted a pilot study of *in situ* bioremediation in a Superfund designated aquifer. The aquifer is in Montana and had been contaminated with wood preservative products; primarily uncontrolled releases, over a 23-year period, of pentachlorophenol and creosote. Pentachlorophenol (PCP) is a chlorinated aromatic compound, and creosote, a derivative of the coal coking operation, contains a complex mix of 270 organic compounds with 16 of these being polynuclear aromatic (PAHs) priority pollutants.[50]

The highest levels of aquifer contamination were found around three areas: the pit where waste materials were dumped, the tank farm that held the PCP and creosote, and the butt dip area where telephone poles were dipped in creosote. The contaminants entered two aquifers (one on top of the other) and migrated as much as a mile downstream. Woodward-Clyde engineers made the decision to first clean the upper aquifer because it posed the greatest potential threat to human health and the environment.

A feasibility study showed that as ground water passed through the contaminated zone, the dissolved oxygen (DO) level dropped off sharply. This indicated that indigenous microorganisms were possibly metabolizing the organic contaminants and in the process using available oxygen. The feasibility study also showed that lack of oxygen became a factor possibly limiting further microbial degradation as the ground water moved farther downstream. Dissolved oxygen has been shown necessary for the degradation of creosote, and PCP can be degraded with or without oxygen.[50] However, an oxygen environment normally produces a faster rate of degradation where PCP

is concerned.[50]

Just as with the Kelly Air Force Base project[42] hydrogen peroxide was used as the means to achieve the necessary DO level in the aquifer. The hydrogen peroxide was injected through converted monitoring wells at a rate of 2.5 liters per second at a concentration of 100 mg/L. Along with hydrogen peroxide addition, nitrogen and phosphorous nutrients were also injected into the aquifer at bimonthly intervals. This aided the microbial activity.

Results of the pilot study showed a reduction in the levels of PCP and PAHs and are shown in Figure 1-18. The DO level rose to almost 20 mg/L five months after hydrogen peroxide injections began while at approximately the same time the pollutant level in the aquifer decreased thus providing

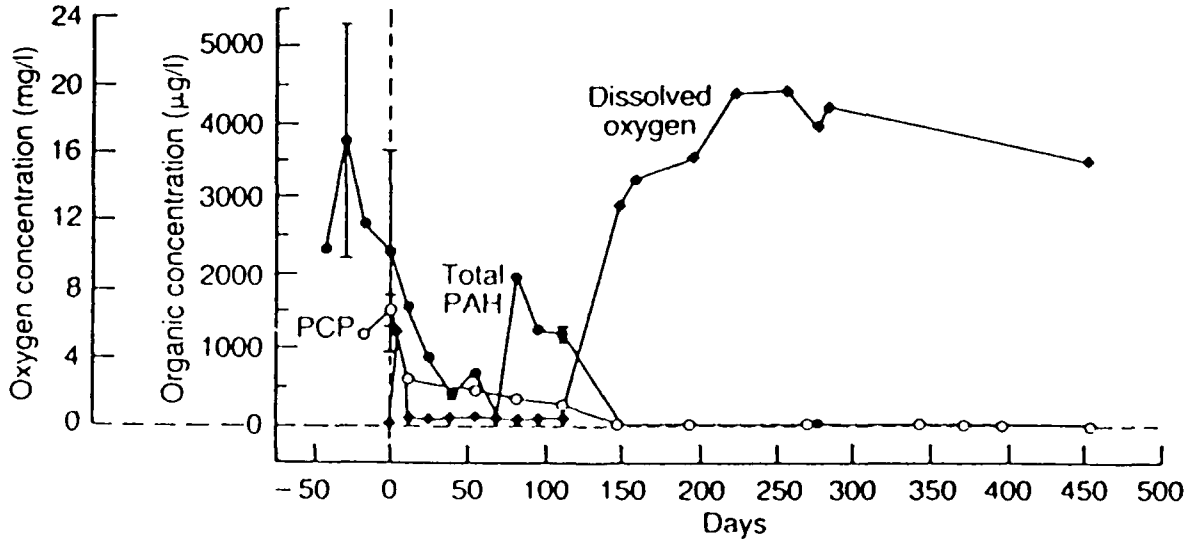


Figure 1-18: Reduction in PCP and PAH Concentrations With A Corresponding Increase In The DO Level[50]

evidence for a biological reduction in the PCP and PAH concentrations. This study provided the first[59] field evidence that oxic conditions could be created within large sections of an aquifer, and the relatively high DO concentration would also coincide with a reduction in organic chemical concentrations. Other evidence for *in situ* bioremediation consisted of an increased density in microbial life and the biological conversion of the nitrate nutrient feed to nitrite.

One of the most important results of this pilot study was the U.S. Environmental Protection Agency (EPA) handed down a record of decision (ROD) concerning the use of *in situ* bioremediation in this aquifer. The ROD mandated the use of *in situ* bioremediation for the full scale clean up; the first such decision by EPA concerning a Superfund aquifer. The full scale *in situ* bioremediation system is scheduled to be in operation by the end of 1990.

Summary and Experimental Objectives

One gallon of ground water out of every 50 gallons is severely contaminated with synthetic organic chemicals.[2,3] Scientists and engineers have turned toward biological means to combat this problem. Canter and Knox'[2] have shown with many cases biological treatment is an effective solution (see Table 1-5). This research and the research of the others described in this report dealt with *in situ* reclamation of contaminated ground water.

The prevailing thought for many years was only the top few centimeters of soil contained any microbial life.[11] Ghiorse and Balkwill'[8] showed in 1983 that as many as one million microbes per gram of soil existed well

existed well below the surface of the ground. Harvey[34] also showed that between 10 and 100 miroorganisms were common on each grain of soil from a Cape Cod aquifer. He showed that 95% of these microorganisms were attached to the soil particles. Harvey[34] thus concluded that an *in situ* biological treatment system would behave as a fixed film system. Life did exist well beneath the ground's surface, but could this life function as an effective remedial measure for ground-water clean up?

Bouwer and McCarty[45] used 3-mm glass beads with a biological film attached in an experimental scale upflow reactor to demonstrate that trace concentrations of 1- and 2-carbon halogenated aliphatic compounds could be degraded. Their experiments were conducted in a methanogenic environment and the aliphatic compounds were fed in with an acetate primary substrate. They achieved a reduction rate of greater than 90% for the aliphatic compounds. Bouwer and McCarty[45] also reported the staged formation of intermediate products during the process of biotransformation. In similar work using 3-mm glass beads and an upflow reactor, Bouwer and Cobb[19] demonstrated that within a laboratory heterotrophic oxidation, denitrification, and sulfate respiration could take place.

Using 6-cm quartzite rocks to form the porous matrix and working under anaerobic conditions, Vogel and McCarty[46] confirmed the formation of intermediate products during the reductive dehalogenation of halogenated aliphatic compounds. This confirmed Bouwer and McCarty's[45] findings with regard to biotransformation stages. Vogel and McCarty[46] hypothesized that through reductive dehalogenation the halogenated aliphatics could be completely mineralized to CO_2, but they did not prove this experimentally.

Parson, *et al.*,[47] also worked with halogenated aliphatics and again confirmed the presence of intermediate products. However their work was performed in static microcosms under reducing conditions. The static microcosms contained genuine aquifer material and thus more closely approximated an underground environment. In similar work that again confirmed the production of intermediate products through reductive dehalogenation, Wilson, *et al.*,[48] worked with methanogenic microcosms.

Wilson, *et al.*,[48] also worked with halogenated aliphatic compounds under methanogenic conditions and with aromatic compounds, the BTX fractions. Microbes were able to degrade the benzene, toluene and xylene but at a relatively slow rate. Majors, *et al.*,[49] used nitrate and molecular oxygen as electron acceptors and were able to degrade the BTX compounds at a faster rate. They too used aquifer material microcosms.

Suflita and Miller[74] continued work with aromatic compounds in microcosms. They established that chlorophenolic compounds could be biodegraded under laboratory conditions. The aquifer material for the microcosms was taken from a designated clean aquifer in Oklahoma. Suflita and Miller[74] performed their experiments under three different conditions: nonmethanogenic anaerobic, methanogenic, and aerobic. The chlorinated phenols were degraded under methanogenic and aerobic conditions, but were not degraded under nonmethanogenic anaerobic conditions.

Work continued in the laboratory while a full scale field study was conducted in West Germany. In the Upper Rhine Graben of West Germany, 20 to 30 tons[71] of spilled hydrocarbons, mostly aliphatic and aromatic compounds, were cleaned to levels that were not harmful to human health and

met German environmental standards. A team of two academic institutions, an engineering firm, and the West German government cooperated in this clean up effort. The reduction in pollutant concentrations after the injection of nitrates and nutrients into the polluted aquifer provided a strong argument for *in situ* biological reclamation.

A field scale project is being conducted by the United States Air Force at Kelly Air Force Base, Texas.[57] Typical organic wastes that polluted the ground water were chlorobenzene, 1,1-dichloroethane, and 1,1-dichloroethylene. Lab scale microcosms and limited field data have encouraged the use of *in situ* biological reclamation, and the Air Force has continued their clean up efforts. Another *in situ* field study, pilot scale, was conducted on a Montana aquifer by Piotrowski[58] and his team from Woodward-Clyde Consultants.

In Montana a 23-year history of uncontrolled disposal resulted in a Superfund site and the contamination of an aquifer by pentachlorophenol and creosote. Hydrogen peroxide was the oxidant used to get oxygen to the microbes underground, and nitrates and phosphorous were nutrients pumped down on a regular basis to aid the biogical remediation process. The result of this pilot study was a significant reduction in contaminant concentrations, and a record of decision was handed down from EPA. The record of decision sanctioned the first full scale clean up of a Superfund site using *in situ* biological remediation techniques. The full scale system is scheduled to be operational by the end of 1990.

Laboratory work has demonstrated an undeniable possibility that *in situ* biological reclamation can be a viable alternative in the spectrum

of ground-water cleanup options. Laboratory work has played an important role in the three previously mentioned field cleanup efforts. Complete and thorough lab studies, while they may be expensive, can save a tremendous amount of time and money in the field. The field efforts also demonstrated *in situ* biological reclamation can be an effective option.

The research effort that follows centered on the development of a better laboratory technique to determine if *in situ* biological reclamation is a viable alternative in a given ground-water cleanup situation. Specifically the objectives of this special research problem were to:

a. Construct and test four triaxial permeability devices for use in ground-water research.

b. Determine the variation of hydraulic conductivity with time and different permeants.

c. Determine the fate of an organic pollutant within a laboratory soil sample.

d. Determine the effects of microbes in a laboratory soil sample on the pollutant effluent concentration.

CHAPTER 2
Methods and Materials

Triaxial Permeability Device Construction

This special research problem centered on the construction and use of four triaxial permeability devices developed by Reid and Williams.[9] Their design drew heavily from a triaxial cell designed and constructed by Dunn, *et al.*[36] Reid and Williams'[9] devices were modified and specifically constructed to meet the exact needs of this special research problem. The primary use of the triaxial permeability device was to determine the permeability or hydraulic conductivity, k, of a given soil sample. The permeability devices were operated simultaneously to obtain a large amount of information in a short time. Triaxial shear tests were not performed as a center load rod was deleted from the design.

The triaxial permeability devices were a variation of the permeameter employed in the standard test, ASTM D 2434-86 Standard Test Method for Permeability of Granular Soils (Constant Head).[35] The primary difference between the ASTM standard permeameter and the triaxial permeability device was a flexible wall membrane. The ASTM permeameter used a rigid wall. The advantage of a flexible membrane over a rigid wall was the flexible membrane allowed *in situ* pressures to be applied to the soil sample. A soil sample could consolidate as it would naturally. A rigid wall permeameter from the ASTM manual is shown in Figure 2-1.

The triaxial permeability device consisted of a primary test cell where an *in situ* soil confining stress was created, a cell pressure reservoir that contained confining fluid, an influent reservoir that

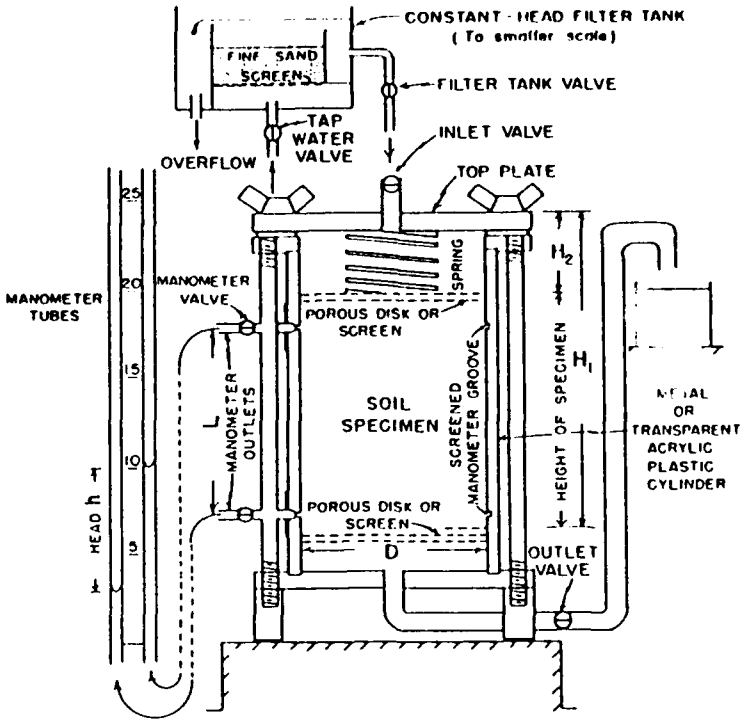


Figure 2-1: ASTM Rigid Wall Permeameter for Granular Soils[35]

contained pore water or permeant for the soil sample, and an effluent reservoir. The effluent reservoir also served as a pressure vessel for creating a pore water pressure or back pressure within the soil sample. Detailed schematic diagrams are presented in Figures 2-2, 2-3, and 2-4. The four permeability devices were constructed on three separate boards. Devices three and four had the capability to be operated separately or simultaneously even though they shared the same board. Device two was modified to include a second influent reservoir so two influents could be introduced at the soil sample simultaneously.

Confining pressure and back pressure were provided by either compressed nitrogen or compressed house air. Permeability devices two, three, and four were pressurized with nitrogen while permeability device one was pressurized with the laboratory compressed-air system. Pressure was regulated to the devices by Fairchild Type 10 regulators. Parker valves controlled direction and rate of liquid and gas flow. Legris

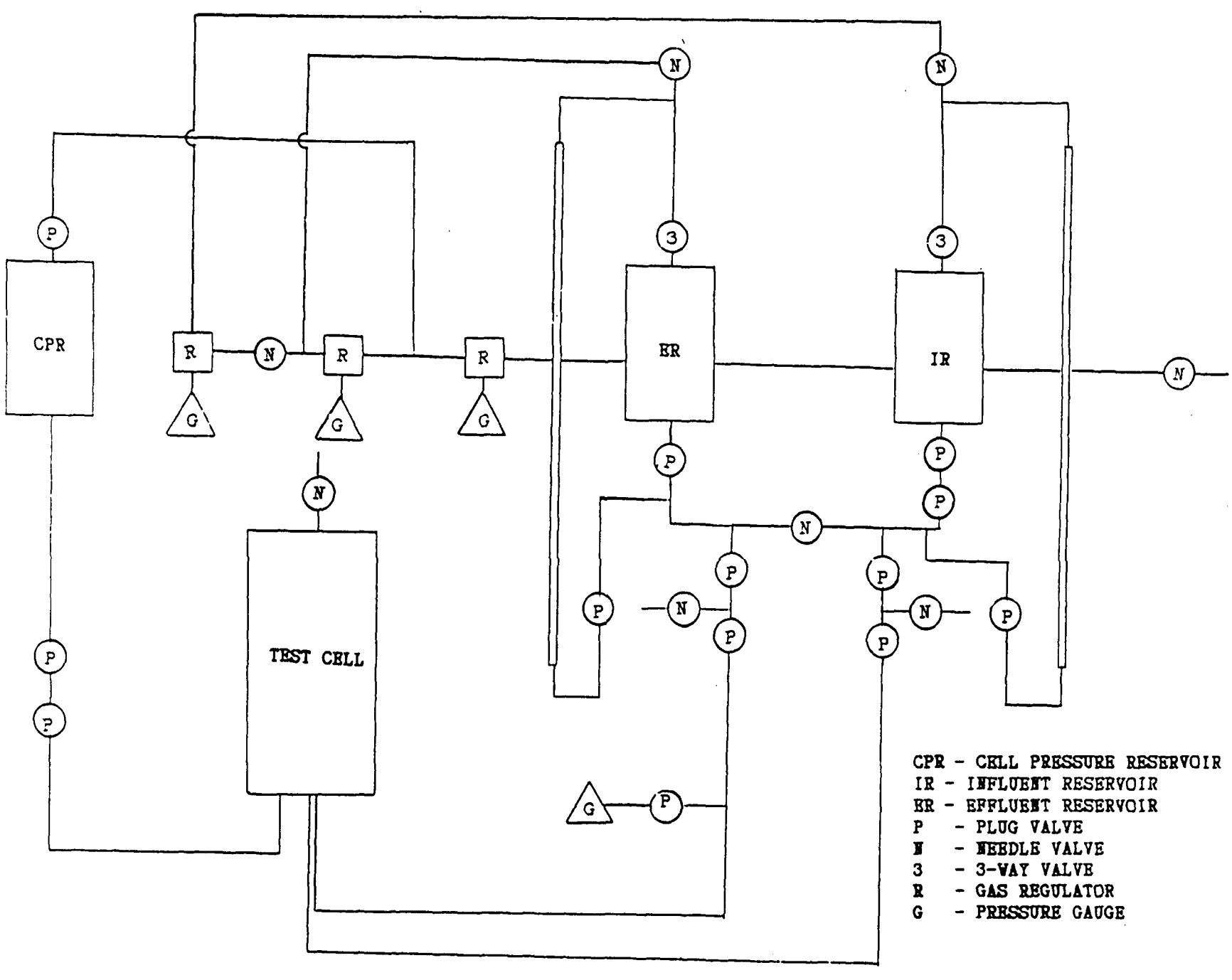


Figure 2-2: Permeameter Board #1

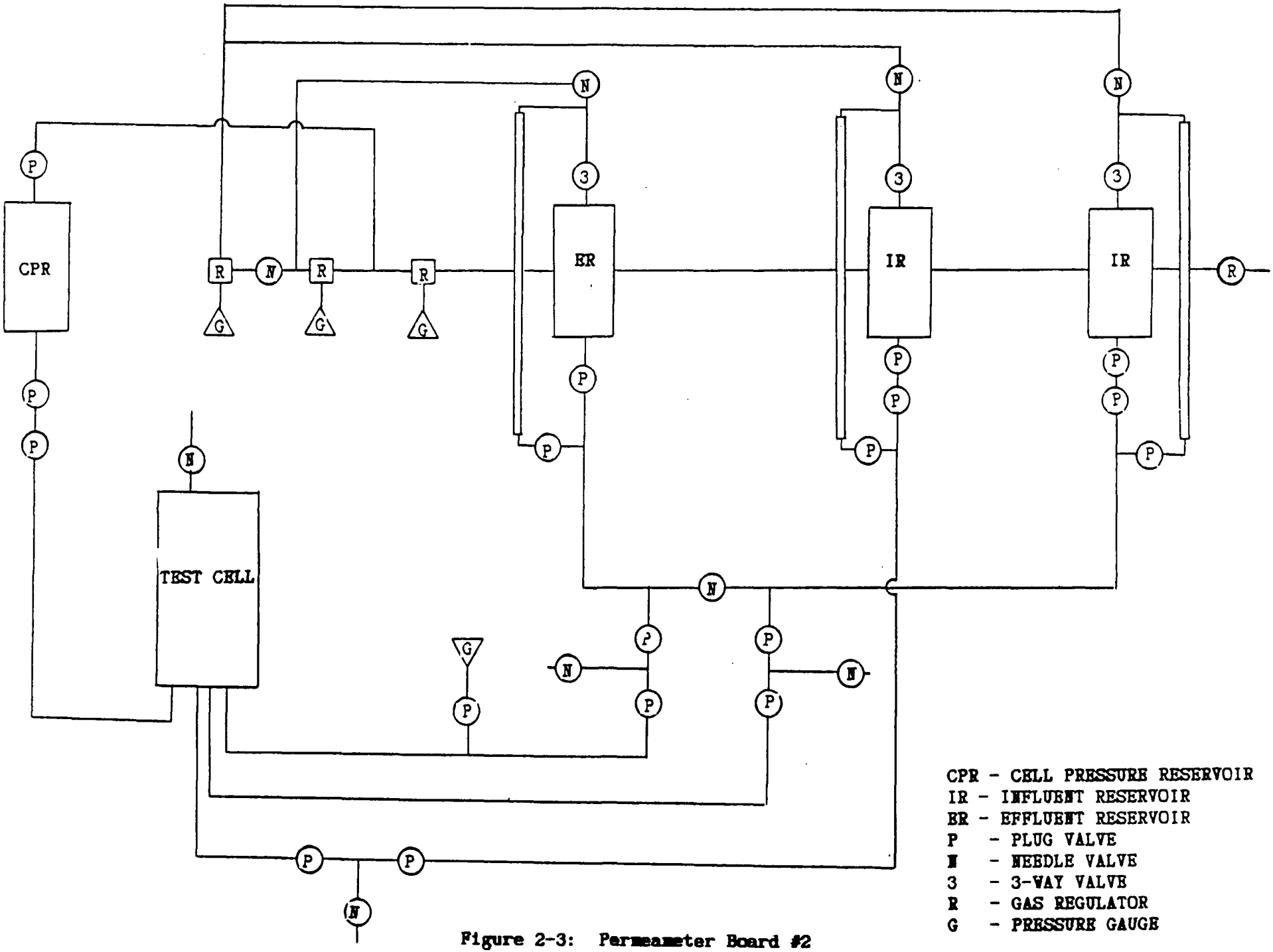


Figure 2-3: Permeameter Board #2

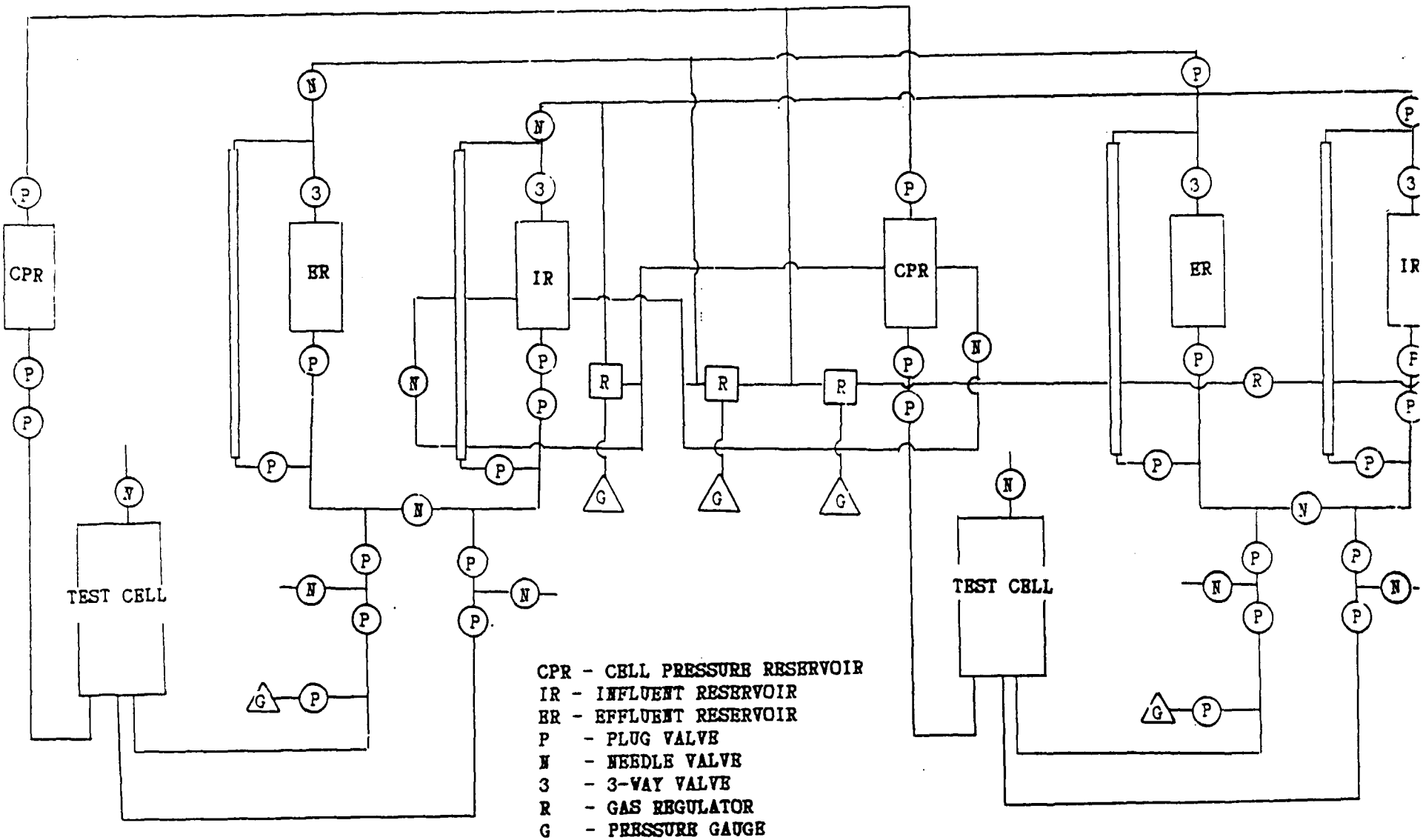


Figure 2-4: Permeameter Boards #3 and #4

flexible plastic tubing was used to connect each devices' reservoirs together. A combination of plastic and Swagelock brass fittings were used to provide transitions from tubing to reservoir or valve. Clear plastic sight tubes (61 cm long) were used to monitor the liquid level and rate of liquid flow during hydraulic conductivity testing.

Top and bottom plates for the primary test cell and reservoirs were cut from 20.3-cm and 15.2-cm extruded aluminum stock, respectively. The reservoir and primary test cell walls were clear acrylic tubing 10.2-cm and 12.7-cm in diameter, respectively (see Appendix B-2 for a drawing of the reservoirs and Appendix B-1 for a detail of the primary test cell with a soil sample). Both the reservoirs and primary test cells were sealed with neoprene rubber O-rings.

All four systems worked identically. Pressurizing gas came in from the source, either nitrogen bottles or house air. The gas was then distributed through the hose system, and pressure was carefully controlled through regulators. The manual opening and closing of valves determined the path and rate of gas and liquid flow. Each individual triaxial permeability testing device was detailed its own set of experiments, but all four operated the same.

Experimental Matrix

The constituents that made up the permeant for the different experimental phases were oxidants, nutrients, and a pollutant. They were then arranged in a matrix so that an orderly experimental progression resulted. The progression of experimental phases is shown in Table 2-1. Each of the four triaxial permeability devices was assigned an oxidant that

Table 2-1: Progression of Experimental Phases

Experimental Codes:

S_0 - contains no microbial seed
S_1 - contains microbial seed
N_0 - contains no nutrients
N_1 - contains nutrients
O_0 - contains no oxidant
O_1 - contains hydrogen peroxide (9 mg/L)
O_2 - contains molecular oxygen (8.5 mg/L)
O_3 - contains nitrates (8.5 mg/L)
P_0 - contains no pollutant
P_1 - contains pollutant (30 mg/L or 100 mg/L)

$S_0N_0O_0P_0$	$S_0N_1O_0P_0$	
$S_0N_0O_1P_0$	$S_0N_1O_1P_0$	
$S_0N_0O_2P_0$	$S_0N_1O_2P_0$	
$S_0N_0O_3P_0$	$S_0N_1O_3P_0$	
$S_0N_0O_0P_1$	$S_0N_1O_0P_1$	No microbes added
$S_0N_0O_1P_1$	$S_0N_1O_1P_1$	
$S_0N_0O_2P_1$	$S_0N_1O_2P_1$	
$S_0N_0O_3P_1$	$S_0N_1O_3P_1$	
$S_1N_0O_0P_0$	$S_1N_1O_0P_0$	
$S_1N_0O_1P_0$	$S_1N_1O_1P_0$	
$S_1N_0O_2P_0$	$S_1N_1O_2P_0$	Microbes added
$S_1N_0O_0P_1$	$S_1N_1O_0P_1$	
$S_1N_0O_1P_1$	$S_1N_1O_1P_1$	
$S_1N_0O_2P_1$	$S_1N_1O_2P_1$	

did not vary through the course of the phases run on that particular permeameter. For the first half of the experiment, Permeameter #1 used molecular oxygen for an oxidant, #2 used no oxidant, #3 used nitrates, and #4 used hydrogen peroxide. Also within the experimental matrix was the introduction of nutrients and a pollutant. The nutrients were nitrogen and phosphorus in 15.0 mg/L and 13.1 mg/L concentrations respectively. The nitrogen and phosphorus sources were 57.2 mg per liter of tap water of ammonium chloride and 1.0 mL of concentrated phosphate buffer as prepared

in the BOD test in *Standard Methods*[13]. When nutrients were required, each amount was mixed with one liter of tap water. The pollutant was 2,4-dichlorophenol, a priority pollutant commonly used as a disinfectant, and found in hospitals, institutions, and food processing plants.[14]

2,4-dichlorophenol was chosen as the organic compound of concern for three reasons. First 2,4-dichlorophenol is a priority polluntant. Second Suflita and Miller[24] showed chlorinated phenols, particularly 2,4-dichlorophenol, to be biodegradable. Last 2,4-dichlorophenol had been shown in through Groff's[27] experiments to be relatively easy to analyze for with UV spectrophotometry. The 2,4-dichlorophenol molecule is shown in Figure 2-5. Physical properties are provided in Table 2-2.

Soil Sample Preparation

Soil samples were formed in the laboratory using Ottawa sand (ASTM C-190) and laboratory grade kaolinite obtained from the geotechnical engineering department. The sand and clay were thoroughly mixed before being poured into a 10.2-cm long cylindrical membrane stretcher that was lined with a latex rubber membrane. Samples were formed within a latex rubber membrane that had been pulled around the membrane stretcher (see Appendix A-1 for detailed instructions of sample formation). The clay was placed in the sample to more closely model an actual field sample. The typical field sample would be expected to have a small amount of clay in it. The average clay fraction was 3.4% on a mass basis. Average soil sample parameters are outlined in Table 2-3. Measurements of sample length and diameter were averaged to arrive at a sample volume. Four measurements were taken with a ruler around the circumference in order to obtain an

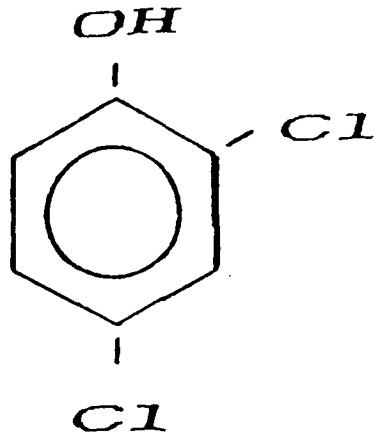


Figure 2-5: 2,4-Dichlorophenol Molecule

Table 2-2: 2,4-Dichlorophenol Physical Properties[28]

Chemical Formula	$Cl_2C_6H_3OH$
Molecular Weight	163.01
Melting Point	45°C
Boiling Point	210°C
Specific Gravity	1.383 @ 25°C
Solubility	4600 mg/L @ 20°C
TOC	0.002 mg/L
Biodegradation*	9 days 100%
Toxicity (rat LD_{50})	0.58 g/kg

* In an aerobic soil suspension with N and P added

average sample height. Three measurements were taken with outside calipers in order to obtain an average sample diameter. The sample mass was read from a Mettler balance to the nearest hundredth of a gram. Density was calculated by dividing the mass by the sample volume. Porosity (volume of voids per unit volume of sample) was calculated by using the total volume and sample density information and assuming the density of individual sand

grains was 2.65 g/cm^3.[2] The density of the clay particles was assumed to be 2.60 g/cm^3.[2]

Table 2-3: Average Soil Sample Parameters

Parameter	Value
Mass	325.05 g
Volume	189.1 cm^3
Bulk Density	1.72 g/cm^3
Height	9.9 cm
Diameter	4.9 cm
Porosity	0.37
Clay Fraction	3.4%

Back Pressure Saturation

After the soil sample was prepared and the cell pressure reservoir was filled (see Appendix A-2), back pressure saturation was initiated. Back pressure saturation was required to remove all gas bubbles from within the sample (Appendix A-3 contains detailed instructions on the procedure for back pressure saturation). During back pressure saturation the soil sample was squeezed from both ends. Pressure was provided by gas through the effluent reservoir. The sample was pressurized to a working effective stress of 103.4 kPa (15 psi). This effective stress was chosen to duplicate the effective stress on a volume of soil 6.5 meters (21.6 ft) below ground. The effective stress was kept constant, but cell pressure and back pressure were raised in order to force more gas bubbles into solution. A graphic of the back pressure saturation concept is shown in Figure 2-6.

The important quantity measured during back pressure saturation was the response of pore pressure to a sudden increase in cell pressure. If a

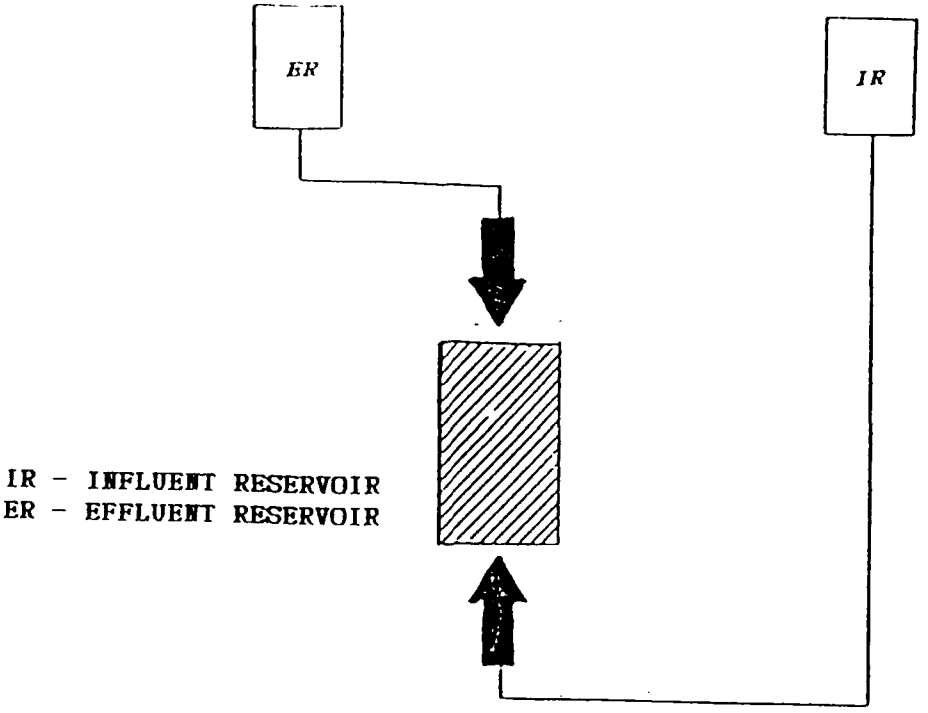


Figure 2 6: Concept of Back Pressure Saturation

sample was entirely saturated, an increase of cell pressure, Δcp, resulted in an increase of pore pressure by Δcp. If a sample was not entirely saturated, pore pressure response would be less than Δcp. The ratio of change in pore pressure over Δcp was taken as the Skempton[9] pore pressure parameter or B value. After back pressure saturation, a sample was isolated by closing appropriate valves and left to consolidate for a 24-hour period. The soil sample was then ready for hydraulic conductivity testing.

Hydraulic Conductivity Testing

Hydraulic conductivity testing was divided into two parts: first with all soil samples having no microbial life and the second with microbial life. Each separate phase of the experiment lasted three days, and hydraulic conductivity measurements were taken each day. The three day period was chosen so that the experimental phases in Table 2-1 would be completed within an available 10-week working period. Each phase of the

experiment was characterized by a particular permeant being passed through the sample to determine the permeant's effect on hydraulic conductivity.

The first half of the hydraulic conductivity testing was conducted on an interval flow basis. Flow only took place when hydraulic conductivity measurements were being taken. The interval flow condition was not a desirable condition and was an unexpected problem during the first half of hydraulic conductivity testing. Ideally a continuous flow of permeant would have been preferred so that the soil sample could have been exposed to as much permenat as possible. The interval flow situation occured because the original triaxial permeability device was designed for a continuous gas source to provide cell pressure and back pressure.

Nitrogen gas was used in three of the devices to achieve anaerobic conditions, and the only source of nitrogen gas was pressurized cylinders. If the permeability devices were left pressurized over night, the nitrogen cylinders would exhaust their capacity. The nitrogen was exhausted because the valves were designed to bleed excess gas pressure into the atmosphere. A redesign of the system that allowed the pressure to be set for the night and then the valves taken out of the loop resulted in a continuous flow system for the second half of the experiment (Appendix A-6 contains detailed instructions for continuous flow operations).

Hydraulic conductivity measurements were done on a "sight glass to sight glass" basis. Valves were arranged so that flow was from the influent sight glass through the sample into the effluent sight glass. A hydraulic conductivity test run consisted of ten or more separate measurements that were then averaged to get a hydraulic conductivity value

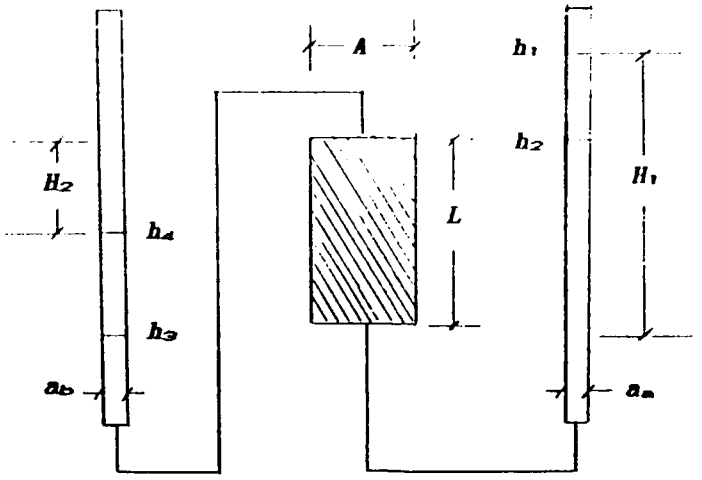
for that particular day. See Appendix A-4 for a thorough description of how hydraulic conductivity measurements were taken.

As put forth in Appendix A-4, each hydraulic conductivity run involved simply measuring the amount of time it took the permeant level in both influent and effluent sight glasses to fall and rise a specified equal distance. The time was recorded and then inserted into a formula that was derived for this particular triaxial permeability device design. The equation is based on Darcy's Law as written in Equation 1-1, and its derivation is shown Figure 2-7.

Microbial Seed

When a microbial seed was required in the progression of experiments, the seed was obtained from a semi-batch reactor set up specifically to grow microbes that could degrade the 2,4-dichlorophenol. The microbial seed for the semi-batch reactor was waste activated sludge obtained from the R.M. Clayton wastewater treatment plant in Atlanta Georgia. The waste activated sludge was 1% to 1.5% suspended solids. The concentration of microbes in the reactor was initially set between 700 mg/L and 1050 mg/L, and the microbes were given a daily diet of 15 mg/L nitrogen as nitrogen, 13.1 mg/L as phosphorous, and 100 mg/L 2,4-dichlorophenol.

In order to get a microbial seed into the soil sample, four 600 ml aliquots were removed from the semi-batch reactor. The aliquots were filterd through a 0.45 μm filter until no fitrate was produced. This procedure left a concentrated biomass on the bottom of the filter paper cup. The contents of the filter paper cup were then slowly poured through qualitative filter paper leaving only a biopaste on the filter paper. The



Initial Conditions

$H_1 = h_1 - h_3$

Final Conditions

$H_2 = h_2 - h_4$

Assume

Outflow = Inflow

Darcy's Law

$$Q = -kiAt \qquad i = H/L$$

$$dQ = -kiAdt$$
$$= a_a(h_1 - h_2)$$
$$= a_b(h_3 - h_4)$$

$$h_4 - h_3 = a_a/a_b(h_1 - h_2)$$

$$H_1 - H_2 = h_1 - h_3 - h_2 + h_4$$
$$\approx h_1 - h_3 + a_a/a_b(h_1 - h_2)$$
$$= (h_1 - h_2)(1 + a_a/a_b)$$

$$dQ = a_a(h_1 - h_2)$$
$$= a_a(H_1 - H_2)/(1 + a_a/a_b)$$
$$= -kHAdt/L$$

$$a_a dH/(1 + a_a/a_b) = -kHAdt/L$$

$$dH/H = -(1/a_a L)kA(1 + a_a/a_b)dt$$

$$\ln H_1/h_2 = kAt(1/La_a)(1 + a_a/a_b)$$

$$k = \{La_a/[At(1 + a_a/a_b)]\} \ln H_1/H_2)$$

Where

$H_1 = h_1 - h_3$

and

$H_2 = h_2 - h_4$

Figure 2-7: Derivation of Hydraulic Conductivity Equation

biopaste was then weighed and stirred into the sand and clay sample. Microbes in the biopaste were mixed into the soil sample as well and as evenly as possible.

Adsorptive Capacity of Soil Samples

Four experiments were run to determine the affect of adsorption on the attenuation of 2,4-dichlorophenol. These experiments along with the triaxial permeability device experiments were designed to demonstrate the difference between adsorptive attentuation and microbial degradation. Two of the four experiments involved measuring the effluent concentration for 2,4-dichlorphenol over an extended period of time. This was done to determine how long it took the soil sample to become saturated, i.e., effluent concentration equaled influent concentration. Hydraulic conductivity measurements were also taken during these experiments. The remaining two experiments involved running an adsorption isotherm. A constant concentration of 2,4-dichlorophenol was added to varying amounts of soil sample material. The soil sample and 2,4-dichlorophenol suspension were then mixed over night. The amount of 2,4-dichlorophenol sorbed to the soil particles was then determined.

The two experiments that attempted to determine the length of time required for a sample to become saturated with 2,4-dichlorophenol were run with influent concentrations of 100 mg/L and 28 mg/L. The soil samples were typical as described in Table 4-3. The 100 mg/L experiment was run over a period of 22 days with 78 samples being analyzed spectrophotometrically. The 28 mg/L sample was run over a period of three days with 21 samples being analyzed. The effluent samples were obtained

identically by the method described in Appendix A-5. The experiment code for both experiments was $S_6N_6O_6P_1$. Samples were taken from the effluent line three to seven times daily.

Before a sample was taken, approximately 100 mL of permeant was forced through the sample by opening the sampling port and closing off the sight glasses and effluent reservoir. This was done in order to flush old permeant out that had been there due to flow stoppage conditions. Approximately 20 mL of sample was taken and then stored in a refrigerator in a tightly sealed bottle. Once a sample was taken, it was analyzed for 2,4-dichlorophenol. For UV analysis, the sample was diluted by a factor of ten (5 mL of sample in 50 mL of tap water), and the pH was increased to near 12 by adding one sodium hydroxide pellet (approximaetly 1 g).

The pH was increased because 2,4-dichlorophenol showed the greatest ability to absorb UV light in the anionic form. The maximum absorbance was found at a wavelength of 239 nm by placing the spectrophotometer in the scan mode and allowing it to plot out an absorbance versus wavelength curve. The plot of absorbance versus wavelength is shown in Figure 2-8. The maximum absorbance of 239 nm was confirmed by Groff's[27] work. She used a value of 240 nm in her work with synthetic resins.

A calibration curve was run in order to have a standard to check the sample absorbance readings. The calibration curve used to obtain sample concentrations is shown in Figure 2-9. In order to get a 2,4-dichlorophenol concentration value, three absorbance readings were taken from one sample and then averaged. This method of concentration determination was used in the sample saturation and adsorption isotherm

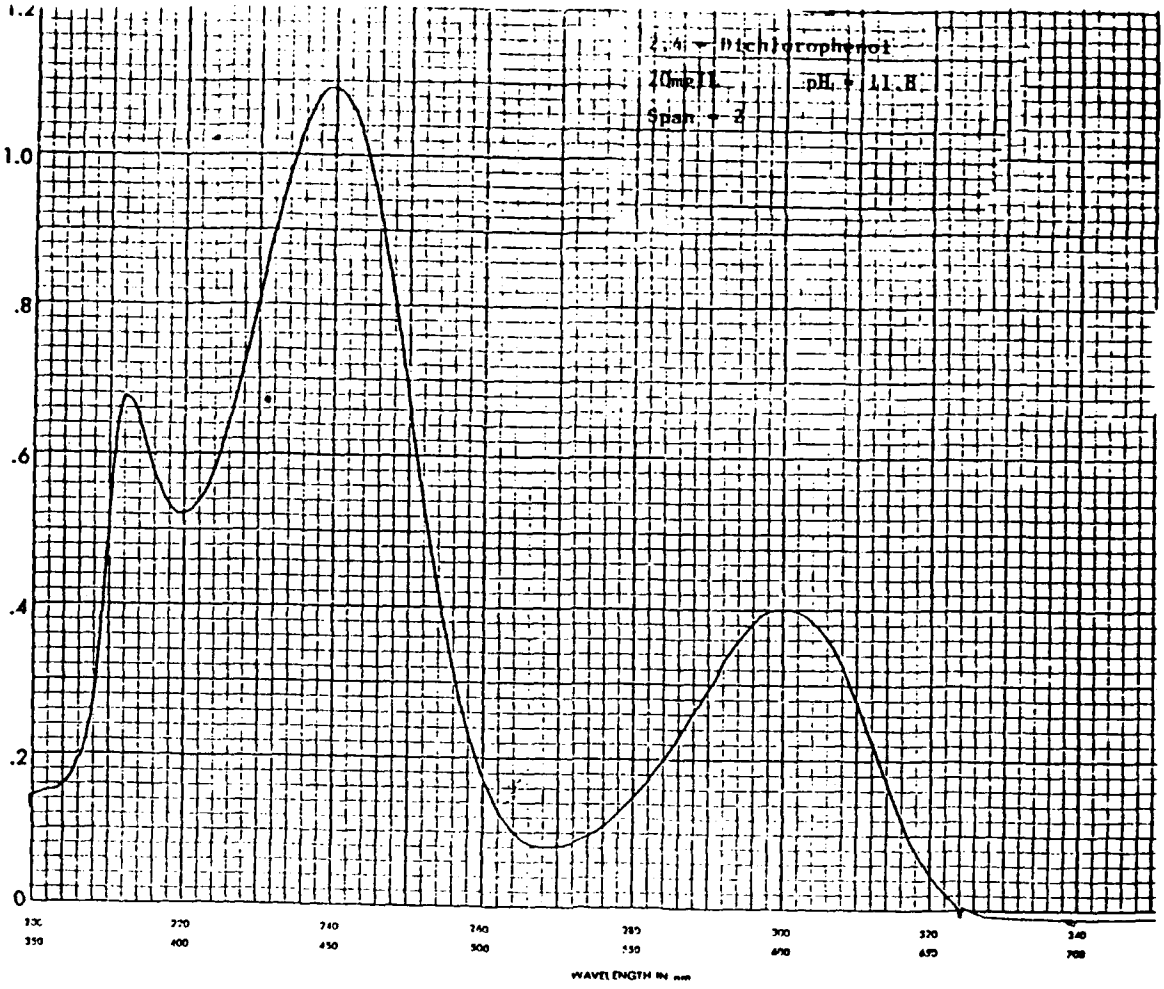


Figure 2-8: Absorbance vs Wavelength for 2,4-Dichlorophenol

experiments.

Two adsorption isotherms were run by varying the amount of soil sample in each bottle and holding the 2,4-dichlorophenol concentration constant. The first isotherm attempt was run at a concentration of 40 mg/L, and the mass of soil varied between 5 grams and 100 grams. Twenty five bottles were used with two of the bottles being blanks with no soil. The second isotherm attempt was run at a concentration of 35 mg/L, and the mass of the soil varied between 5 grams and 20 grams. This experiment also used 25 bottles, but five of the bottles were blanks without soil. Results of the first isotherm experiment necessitated the changes in the second experiment. After being shaken overnight (10 hours), the contents of the bottles were filtered, and the filtrate was analyzed for 2,4-dichlorophenol

spectrophotometrically. The same method was also used to determine the 2,4-dichlorophenol concentration in the sample saturation experiments. Changes in concentration if any were then converted to a mass of 2,4-dichlorophenol adsorbed onto the soil particles. The mass data was then plotted as an isotherm.

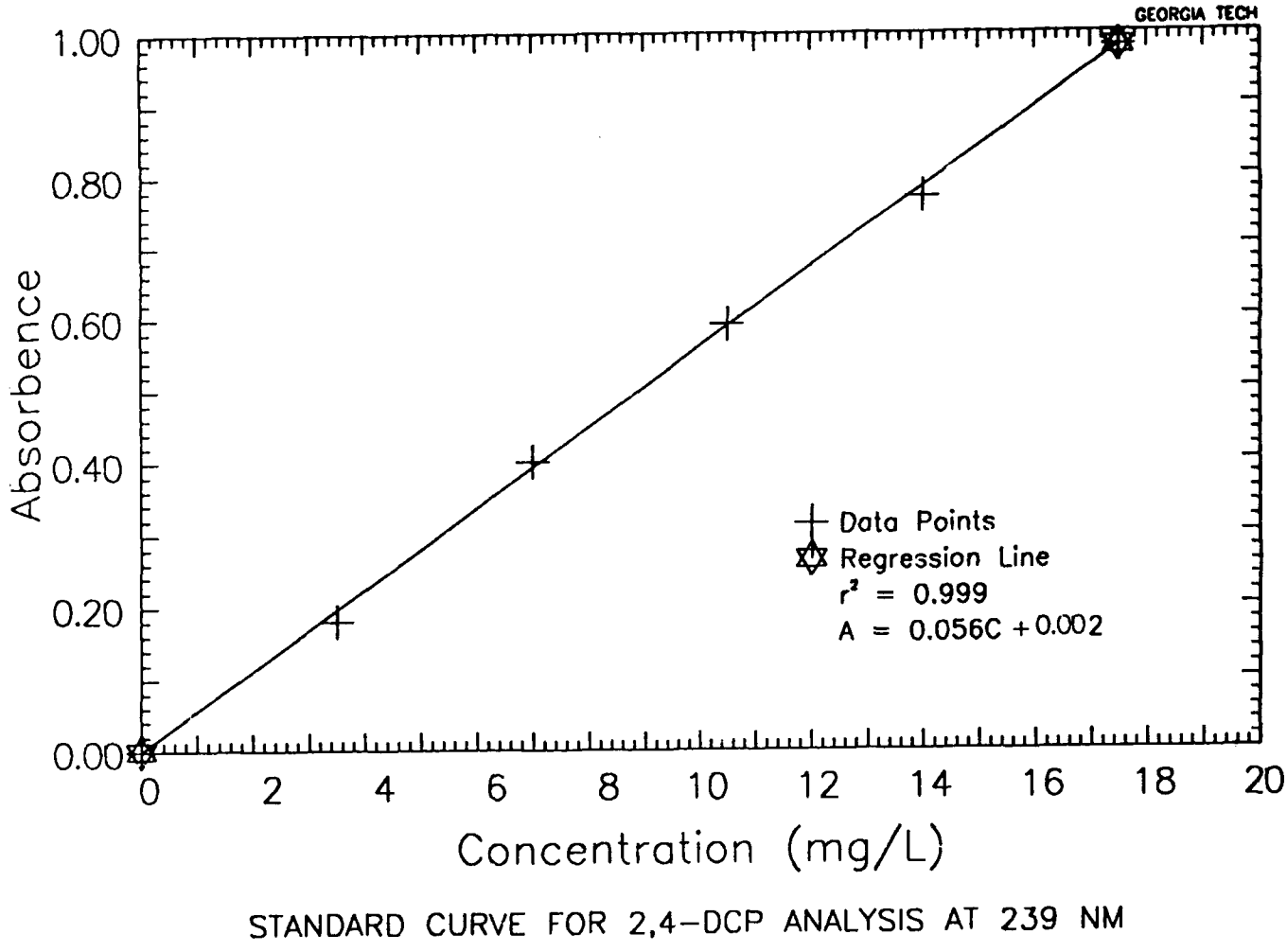


Figure 2-9: UV Calibration Curve for 2,4-Dichlorphenol

CHAPTER 3
Experimental Results

Six months were devoted to design and construction of four triaxial permeability devices. All materials were purchased from vendors, and raw stock was machined to design specifications as shown in Appendix B-1. Once constructed all valves, regulators, gauges, reservoirs, test cells, and tubing were pressure tested well above normal working pressures. The testing and experimentation phase lasted approximately two and a half months with hydraulic conductivity, microbial attenuation, adsorption break through curve, and adsorption isotherm experiments being conducted.

Hydraulic conductivity experiments were performed according to the schedule of experimental codes found in Table 2-1. The objective was to observe changes in hydraulic conductivity as the permeant was changed according to a schedule. The schedule was used to have a consistent amount of time for each experiment and to keep the experiments moving steadily.

In order to determine the variation of hydraulic conductivity with time and permeant, experimental runs were made according to procedures outlined in Appendix A-4. Each hydraulic conductivity versus time data point resulted from averaging individual hydraulic conductivity runs. The number of individual hydraulic conductivity runs per data point averaged out to ten. The standard deviation for individual hydraulic conductivity runs was normally, 86% of the time, less than 10%. The remaining standard deviations varied between 11% and 48%.

Testing Triaxial Permeability Devices

Upon completion of construction, pneumatic and hydraulic lines were tested to three times their normal operating pressure, 103.4 kPa (15 psi). Leaks and weak points in the system were immediately repaired and retested. Spare parts were purchased for future use in the triaxial permeability devices.

The triaxial permeability devise design proved to be flexible. For example, a problem immediately developed with the devices' ability to run continuously on nitrogen gas. Nitrogen gas was provided from individual cylinders, and the gas regulators were the type that bled excess gas continuously to the atmosphere. Over night, even after the regulators had been carefully set, much of the nitrogen in the cylinder was wasted into the atmosphere. By changing the flow arrangement in the pneumatic lines, the system was charged in the evening and operated overnight without wasting nitrogen. Once the sytems ran continuously, more meaningful data was taken. The four devices also had the capability to be expanded and altered; influent and effluent reservoirs could be enlarged by changing to a taller plexiglass cylinder. Over two and a half months of daily data taken from the devices demonstrated a successful design and construction effort.

Hydraulic Conductivity vs Time

Hydraulic conductivity data was taken over a two and a half month period. Graphs illustrate hydraulic conductivity as it changed on a daily basis, and are arranged in a series of related pairs. Each pair relates to a single soil sample. The first of the related graphs

illustrates how hydraulic conductivity changed with time. The second graph illustrates the volume of pore fluid that flowed through the soil sample for that series of hydraulic conductivity runs. A series of runs involved changing the permeant three times per soil sample. Four different permeants were run through the sample for three days; this 12 day sequence was a normal series of hydraulic conductivity runs. However, if flow was adequate, one to three extra days of data was gathered using the last permeant. Permeant changes can be followed in the graph by matching the symbols with the key. A full explanation of the experiment codes and the progression of experiments can be found in Table 2-1.

The volume of fluid passed through a soil sample was measured in terms of pore volumes. Pore volume is the volume of voids in a soil sample capable of containing permeant. Pore volumes were calculated, as related in Chapter 2, by first calculating porosity (volume of voids per unit volume of sample) and then multiplying porosity by the total soil sample volume.

Neither the hydraulic conductivity nor permeant flow graphs have their time axis beginning with day "zero". Day zero was used to back pressure saturate the sample and prepare it for the tests. The amount of permeant used to back pressure saturate the sample was counted toward the total amount of permeant passed. Therefore "t_0", Day 1, was the point where the first hydraulic conductivity measurement was taken.

The first experimental data shown in Figures 3-1 and 3-2 was taken from triaxial permeability device #1. The oxidant for device #1 was

molecular oxygen, O_2. This system was powered by the laboratory compressed air system and it provided oxygen for the experiments. This first series of hydraulic conductivity experiments on triaxial permeability device #1 had to be run on an intermittent flow basis. There were three other hydraulic conductivity experiments run simultaneously, and even though device #1 could have run continuously, the others could not. Device #1 was run on an intermittent basis so a valid comparison could be made among all four devices.

Results of the first hydraulic conductivity runs are presented in Figure 3-1. Molecular oxygen was the constant oxidant and there was no microbial seed. Nutrients were added on day 4 and day 10. 2,4-dichlorophenol was added into the permeant on day 7. Before the permeant change was made on day 7, an extra hydraulic conductivity run

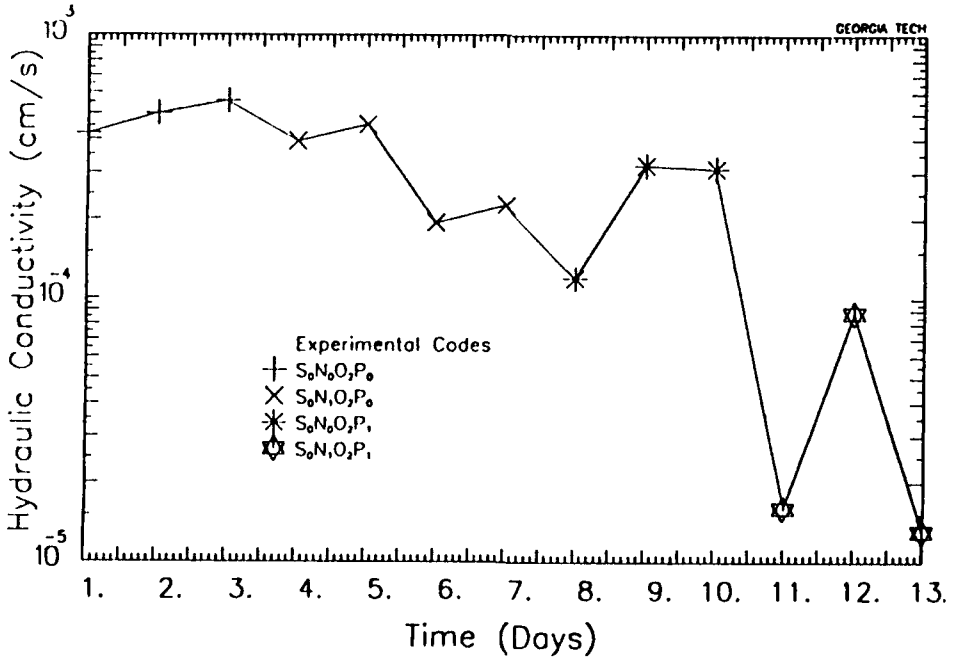


Figure 3-1: Hydraulic Conductivity vs Time (Without Microbial Seed and O_2 As A Constant On Perm Bd #1)

was made using no pollutant. This was performed as a quick check on the previous day's data because it was the first series of hydraulic conductivity runs. All other extra runs that deviated from the normal three day series with the same permeant were carried out at the end of each series.

Hydraulic conductivity decreased 97% over 13 days. This decrease was erratic and unpredictable. Only during days 2 and 3 and days 10 and 11 did hydraulic conductivity change in the same way by increasing and decreasing respectively. The remainder of the time was given to one day trends, either increase or decrease, that would change on the next day. However, the overall trend was a decrease in hydraulic conductivity. All three changes in permeant resulted in a decrease in hydraulic conductivity.

The initial constant rate of flow through the soil sample as shown in Figure 3-2 was due to intermittent flow conditions. A constant amount of permeant was passed through the soil sample each day so hydraulic conductivity data could be taken. Continuous flow in permeability device #1 was initiated temporarily on day 9 because an effort was made to remedy the nitrogen problem with the other three triaxial permeability devices. This caused the volume passed through the sample to increase. That effort was unsuccessful and intermittent flow was resumed the next day with the initial flow rate. The pore volume of the soil sample used for the experimental results shown in Figures 3-1 and 3-2 was 61.0 mL. In all, 685.1 mL of permeant passed through this soil sample.

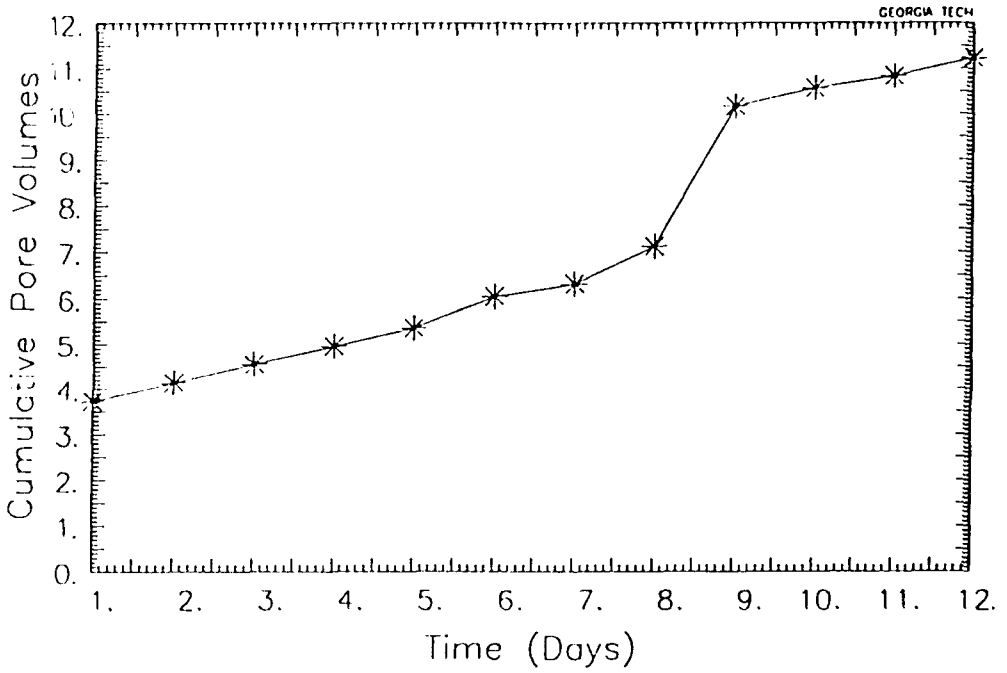


Figure 3-2: Permeant Flow in Pore Volumes Corresponding to Experiment Shown in Figure 3-1

Table 3-1: Standard Deviations for All Data Points Contained in Figure 3-1

Experiment Code	Date of HC Run (Day)	K_{avg} (cm/s x 10^{-4})	S_K (cm/s x 10^{-5})
S..N..O..P..	1/12/88 (1)	4.21	2.73 (6%)
	1/13/88 (2)	5.01	8.94 (18%)
	1/14/88 (3)	5.59	5.59 (10%)
S..N..O..P..	1/15/88 (4)	3.95	2.84 (7%)
	1/16/88 (5)	4.55	3.24 (7%)
	1/17/88 (6)	1.94	8.26 (42%)
	1/18/88 (7)	2.27	6.86 (30%)
S..N..O..P..	1/18/88 (8)	1.20	4.11 (34%)
	1/19/88 (9)	3.22	11.0 (34%)
	1/20/88 (10)	3.13	1.87 (6%)
S..N..O..P..	1/21/88 (11)	0.16	0.19 (12%)
	1/22/88 (12)	0.88	0.65 (7%)
	1/23/88 (13)	0.13	0.07 (5%)

As mentioned previously, the standard deviation for all data was normally 10% or less. Standard deviations, S_K, and values for data points, K_{avg}, from Figure 3-1 are highlighted in Table 3-1.

From permeability device #1, results of the second hydraulic conductivity series using molecular oxygen are shown in Figure 3-3. A microbial seed was added to this soil sample. Nutrients and pollutant were added at the same times as the first sample. Hydraulic conductivity decreased 35% over the 15 days the experiment was run. The decrease was erratic but two three day trends, both decreasing, were seen for days 2, 3 and 4, and days 6, 7 and 8. Two of the three changes

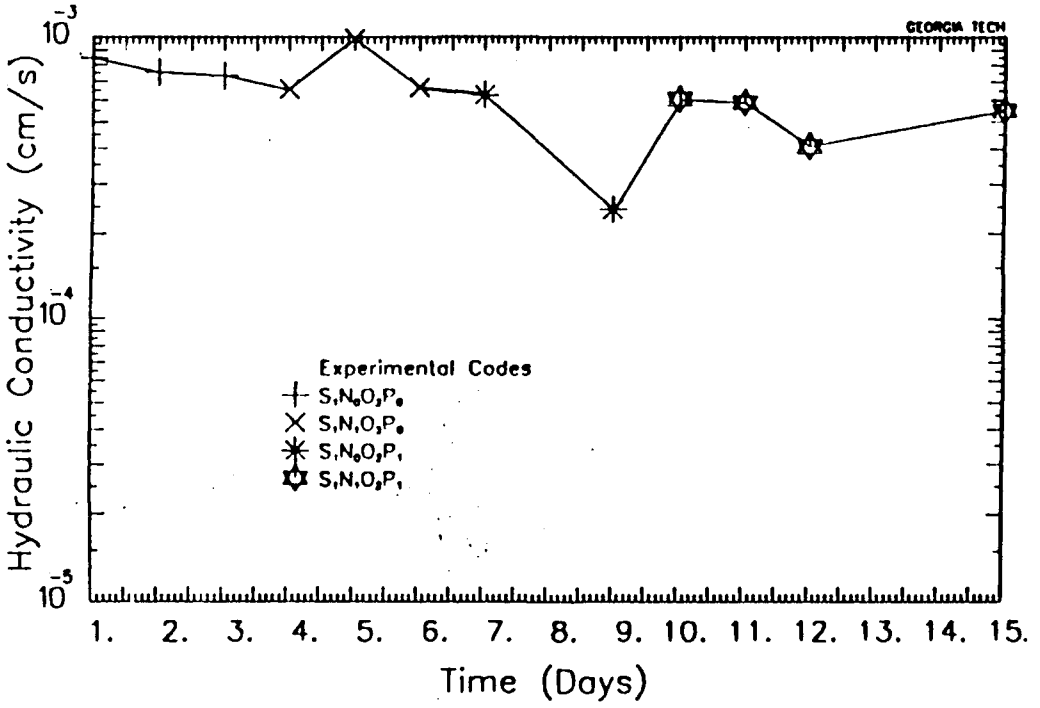


Figure 3-3: Hydraulic Conductivity vs Time (With Microbial Seed and O_2 As A Constant On Perm Bd #1)

in permeant resulted in a decrease in hydraulic conductivity.

By the time experimental results shown in Figure 3-3 were recorded, the intermittent flow problem with the nitrogen driven permeability devices had been solved. This accounts for an order of magnitude difference in pore volumes of permeants passed through the samples in

Figures 3-2 and 3-4. As seen in Figure 3-4, permeant flow began at a rate of nine pore volumes per day for the first seven days. On day 8 no flow was measured as noted in Table 3-3. By days 10 and 11, permeant flow rate had increased as had hydraulic conductivity. This sample's pore volume was 58.5 mL, and 7055.1 mL of permeant passed through it.

Table 3-2 contains the values for the data points and the standard deviations of the data contained in Figure 3-3.

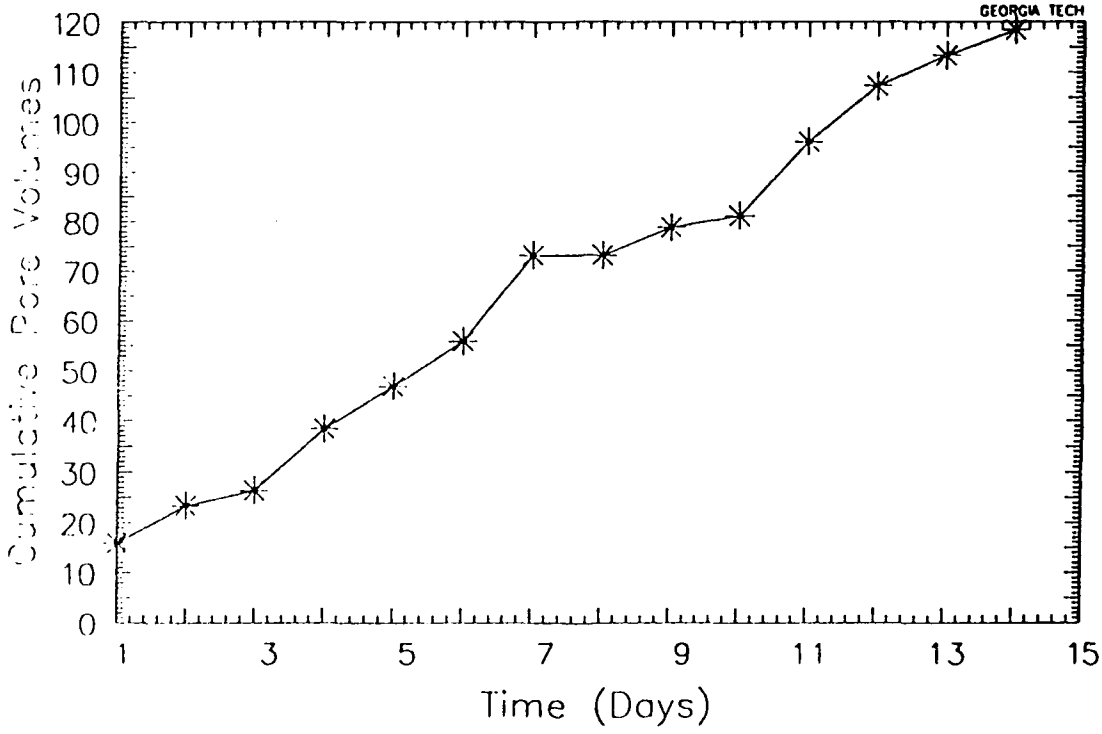


Figure 3-4: Permeant Flow in Pore Volumes Corresponding to Experiment Shown in Figure 3-3

The next set of experimental results, Figures 3-5 through 3-8, were experiments run with no oxidant. However they were run on different permeameter boards. Originally all like pairs of experiments, same oxidant, with and without microbes, were to be run on the same permeameter board. An additional requirement to run an adsorption

Table 3-2: Standard Deviations for All Data Points Contained in Figure 3-3

Experiment Code	Date of HC Run (Day)	K_{avg} (cm/s x 10^{-4})	S_K (cm/s x 10^{-5})
$S_1N_1O_0P_0$	2/14/88 (1)	8.46	2.43 (3%)
	2/15/88 (2)	7.53	3.18 (4%)
	2/16/88 (3)	7.33	16.5 (22%)
$S_1N_1O_1P_0$	2/17/88 (4)	6.57	5.65 (8%)
	2/18/88 (5)	9.87	5.65 (6%)
	2/19/88 (6)	6.66	3.98 (6%)
$S_1N_1O_1P_1$	2/20/88 (7)	6.25	2.57 (4%)
	2/21/88 (8)	----	----
	2/22/88 (9)	2.45	1.22 (5%)
$S_1N_1O_2P_1$	2/23/88 (10)	6.06	5.10 (8%)
	2/24/88 (11)	5.89	3.34 (6%)
	2/25/88 (12)	4.09	1.04 (2%)
	2/28/88 (15)	5.48	2.76 (5%)

---- Did not make run

breakthrough experiment interrupted this progression. The experiment represented by Figure 3-5 was run on permeater board #2 and the experimental results shown in Figure 3-7 were obtained from permeameter board #3.

Hydraulic conductivity results with a permeant which contained no oxidant and no microbes are presented in Figure 3-5. Nutrients were added on day 4 and 10, and 2,4-dichlorophenol was added on day 7. Hydraulic conductivity decreased 36% over the 12-day period. There was one three day period of consistent results; days 2, 3 and 4 showed an increase in hydraulic conductivity. Any other daily hydraulic conductivity trends lasted two days or less. All three permeant changes resulted in a hydraulic conductivity increase.

The relatively constant rate of flow shown in Figure 3-6 reflects intermittent flow conditions. An average of 1.15 pore volumes of

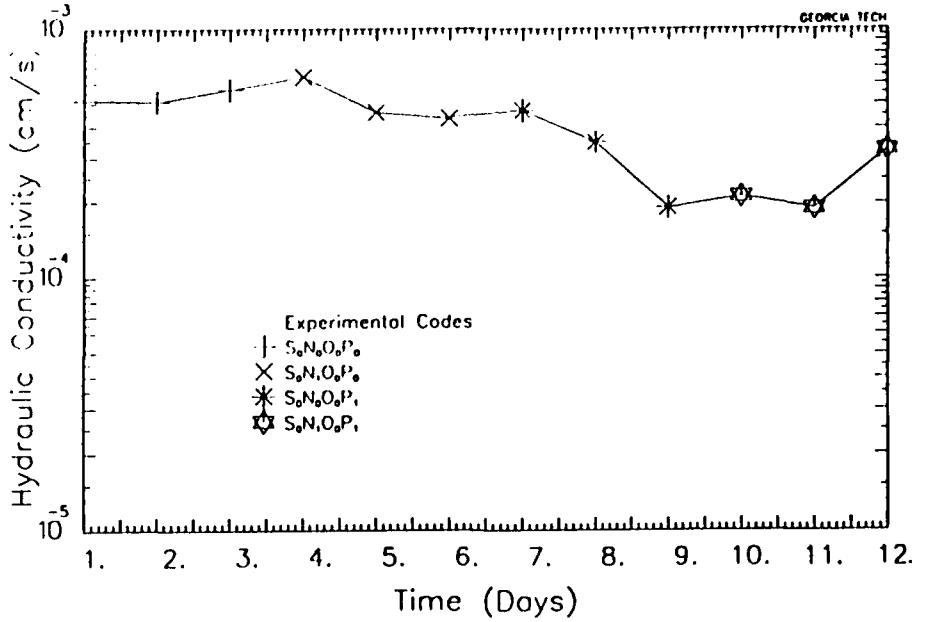


Figure 3-5: Hydraulic Conductivity vs Time (Without Microbial Seed and No Oxidant As A Constant On Perm Bd #2)

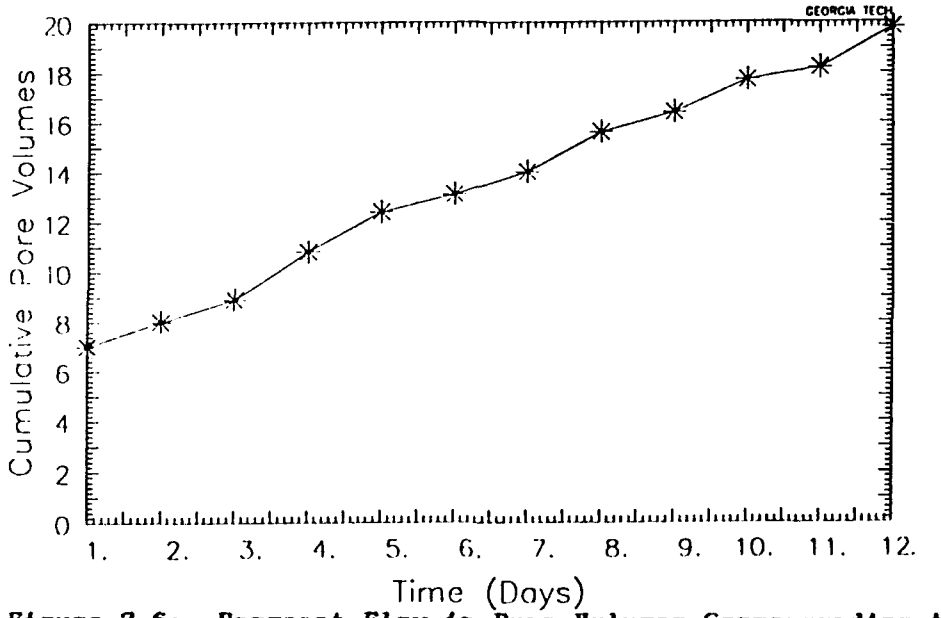


Figure 3-6: Permeant Flow in Pore Volumes Corresponding to the Experiment Shown in Figure 3-5

permeant flowed through the sample each day that hydraulic conductivity data was taken. The pore volume of the soil sample used for the data in Figures 3-5 and 3-6 was 74.6 mL, and 1474.2 mL of permeant passed through the sample.

Table 3-3 contains the values for the data points and the standard deviations of the data contained in Figure 3-5.

Table 3-3: Standard Deviations for All Data Points Contained in Figure 3-5

Experiment Code	Date of HC Run (Day)	K_{avg} (cm/s x 10^{-4})	S_K (cm/s x 10^{-5})
S.N.O.P.	1/22/88 (1)	5.17	1.17 (2%)
	1/23/88 (2)	5.09	2.62 (5%)
	1/24/88 (3)	5.69	2.65 (5%)
S.N.O.P.	1/25/88 (4)	6.38	2.57 (4%)
	1/26/88 (5)	4.61	2.57 (6%)
	1/27/88 (6)	4.36	1.38 (3%)
S.N.O.P.	1/28/88 (7)	4.69	1.92 (4%)
	1/29/88 (8)	3.51	1.62 (5%)
	1/30/88 (9)	1.91	0.80 (4%)
S.N.O.P.	1/31/88 (10)	2.12	0.98 (5%)
	2/1/88 (11)	1.90	0.69 (4%)
	2/2/88 (12)	3.28	15.7 (48%)

Experimental values for the second series of hydraulic conductivity that contained no oxidant are shown in Figure 3-7. A microbial seed was continuously present in this soil sample. Nutrients were added on days 4 and 10. The pollutant 2,4-dichlorophenol was added on day 7. Hydraulic conductivity shown in Figure 3-7 decreased 93% in the 15 days data was gathered. The trend was a relatively consistent decrease in hydraulic conductivity over time. Only the hydraulic conductivity readings for days 8 and 12 interrupted the downward trend. Two of the three permeant changes resulted in a decrease in hydraulic conductivity. It did not vary for the third permeant change.

The changes in permeant flow shown in Figure 3-8 did not match well with the changes in hydraulic conductivity shown in Figure 3-7. This was a continuous flow experiment characterized by sudden increases in flow rate followed by three or four days of constant flow. This happened three times. No correlation can be made between the increases

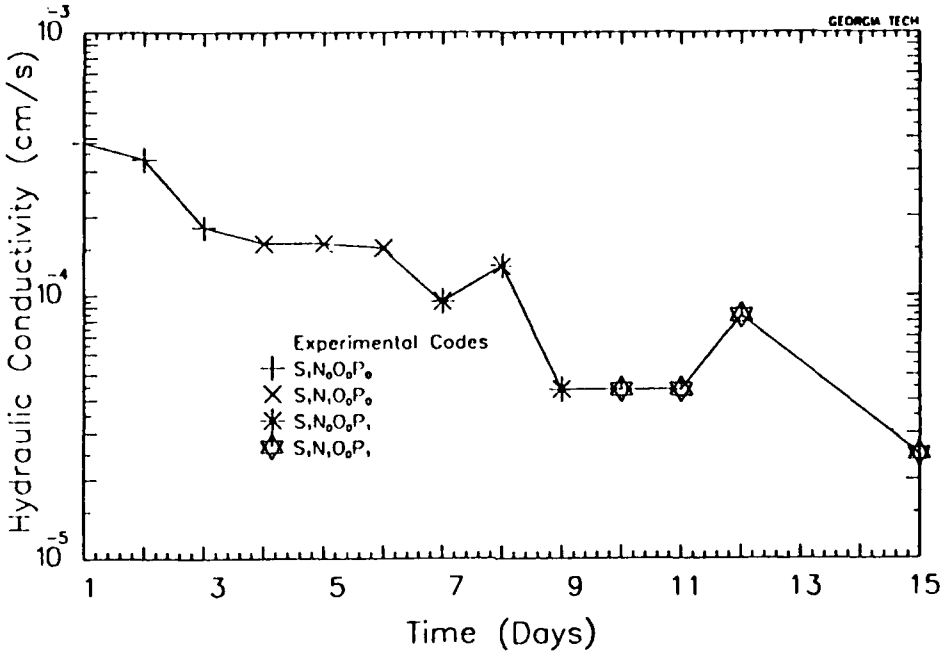


Figure 3-7: Hydraulic Conductivity vs Time (With Microbial Seed and No Oxidant As A Constant On Perm Bd #3)

in flow rate between days 7 and 11 and an increase in hydraulic conductivity. Hydraulic conductivity was decreasing on day 7 and remained constant for days 9 through 11. However the following day, days 8 and 12 respectively, each case witnessed an increase in hydraulic

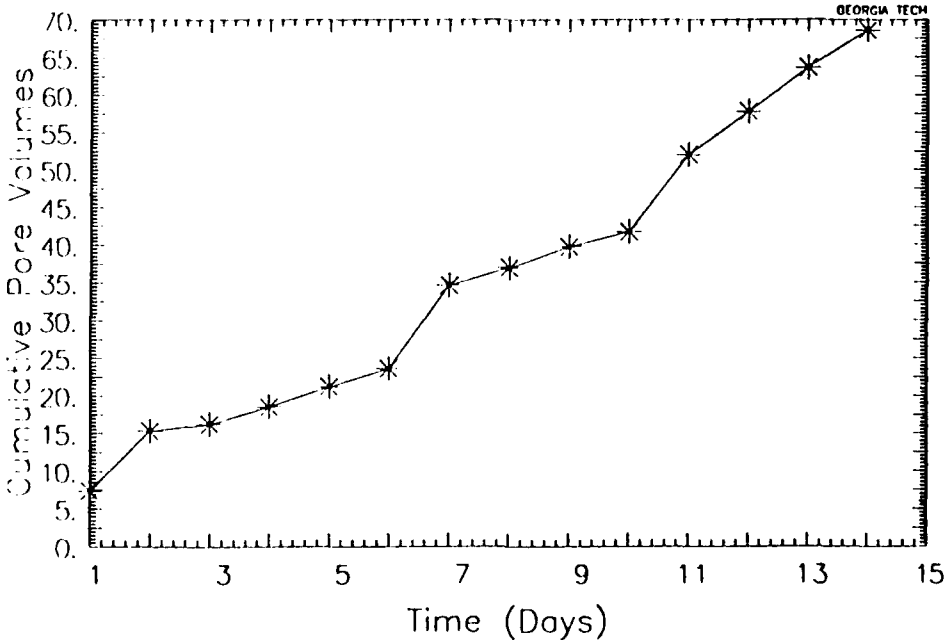


Figure 3-8: Permeant Flow in Pore Volumes Corresponding to the Experiment Shown in Figure 3-7

conductivity. The pore volume of the soil sample in the experiment represented by Figures 3-7 and 3-8 was 55.5 mL, and 3936.6 mL of permeant passed through this sample.

Table 3-4 contains the values for the data points and the standard deviations of the data contained in Figure 3-7.

Table 3-4: Standard Deviations for All Data Points Contained in Figure 3-7

Experiment Code	Date of HC Run (Day)	K_{avg} (cm/s x 10^{-4})	S_K (cm/s x 10^{-5})
S,N,O,P,	2/14/88 (1)	3.84	8.56 (22%)
	2/15/88 (2)	3.32	2.27 (7%)
	2/16/88 (3)	1.82	2.01 (11%)
S,N,O,P,	2/17/88 (4)	1.58	2.61 (16%)
	2/18/88 (5)	1.58	2.61 (16%)
	2/19/88 (6)	1.52	0.53 (3%)
S,N,O,P,	2/20/88 (7)	0.95	0.97 (10%)
	2/21/88 (8)	1.29	0.82 (6%)
	2/22/88 (9)	0.44	0.33 (8%)
S,N,O,P,	2/23/88 (10)	0.44	0.23 (5%)
	2/24/88 (11)	0.66	0.21 (3%)
	2/25/88 (12)	0.84	0.38 (4%)
	2/28/88 (15)	0.25	0.12 (5%)

The hydraulic conductivity experiment performed with nitrates as the oxidant is shown in Figure 3-9. This experiment was performed on permeameter board #3. Unfortunately the nitrate experiment was not repeated with microbes in the sample because of the additional breakthrough experiment mentioned earlier. The hydraulic conductivity decreased 36% during the experiment. The first half of this particular experiment showed a two day trend of decreasing hydraulic conductivities. This was followed by a three day trend of increasing hydraulic conductivity values that rose above the initial value, 3.14 x 10^{-4} cm/s. The second half of the experiment was a consistent six-day

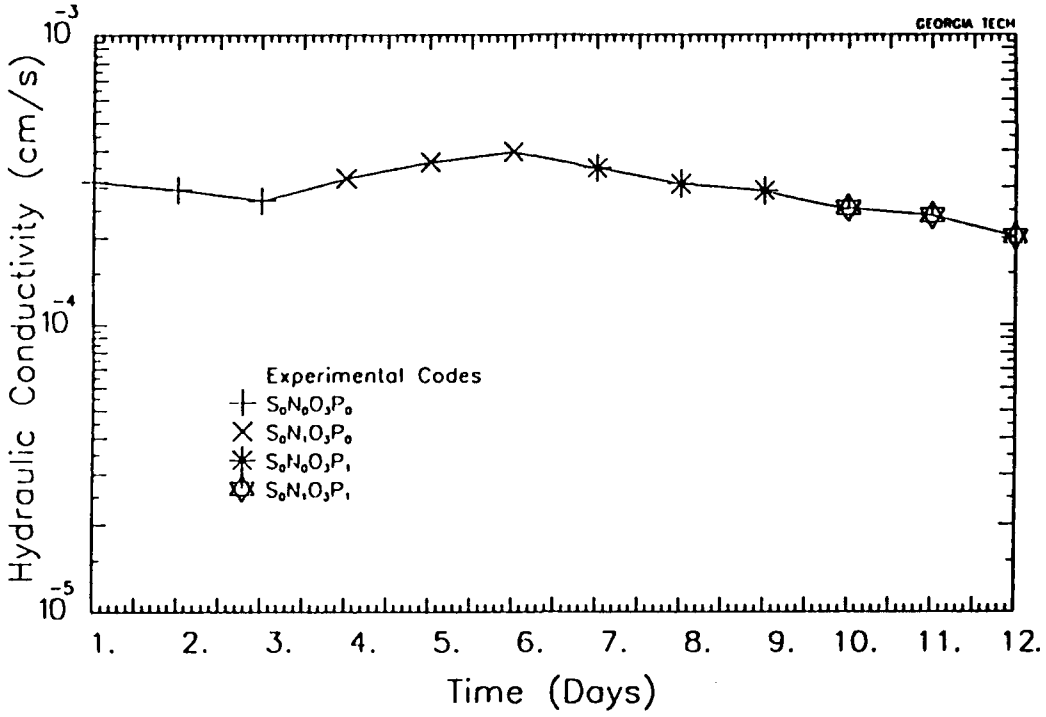


Figure 3-9: Hydraulic Conductivity vs Time (Without Microbial Seed and Nitrates As A Constant On Perm Bd #3)

decrease in hydraulic conductivity. Two out of three permeant changes resulted in a decrease in hydraulic conductivity.

Permeant flow for the experiment represented by Figures 3-9 and 3-10 was under intermittent flow conditions. As seen in Figure 3-10, the flow rate increased at the day six point because more hydraulic conductivity data runs were made for each data point in Figure 3-9. At this point, relatively high hydraulic conductivity values (> 3.14×10^{-4} cm/s) provided an opportunity to make more runs thus increasing permeant passed through the sample. The pore volume of the soil sample used in the nitrate experiment was 78.8 mL, and 1911.6 mL of permeant passed through it.

Table 3-5 contains the values for the data points and the standard deviations of the data contained in Figure 3-9.

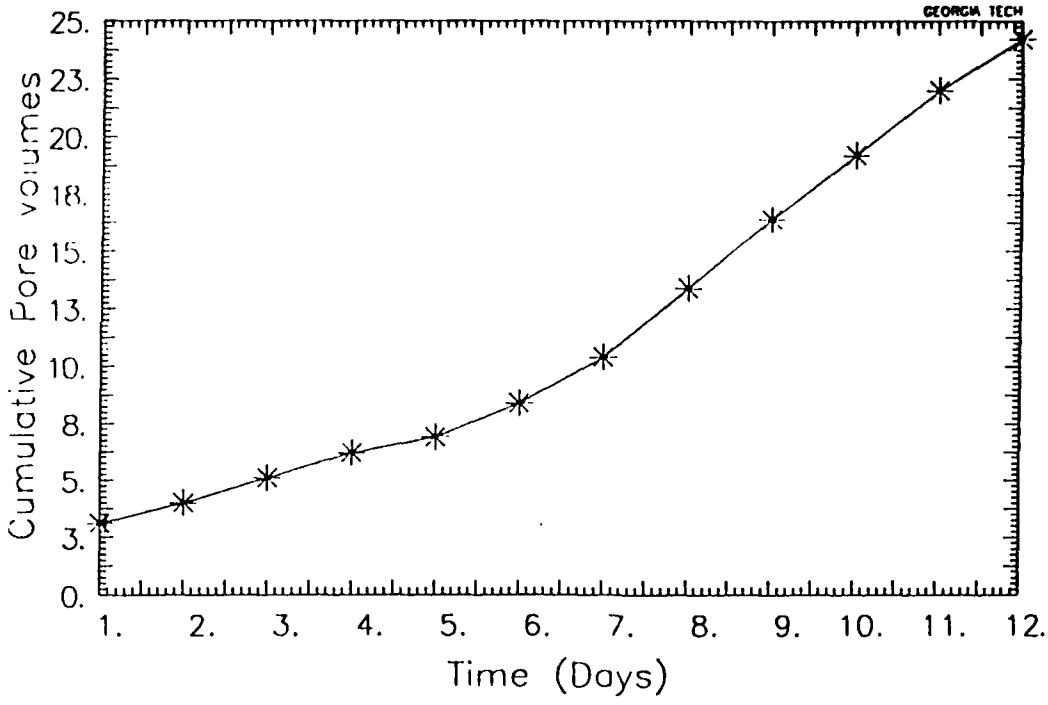


Figure 3-10: Permeant Flow in Pore Volumes Corresponding to the Experiment in Figure 3-9

Table 3-5: Standard Deviations for All Data Points Contained in Figure 3-9

Experiment Code	Date of HC Run (Day)	K_{avg} (cm/s x 10^{-4})	S_K (cm/s x 10^{-5})
S.N.O.P.	1/22/88 (1)	3.14	0.69 (2%)
	1/23/88 (2)	2.94	2.02 (7%)
	1/24/88 (3)	2.70	0.68 (2%)
S.N_1O.P.	1/25/88 (4)	3.22	1.02 (3%)
	1/26/88 (5)	3.66	1.77 (5%)
	1/27/88 (6)	3.98	1.07 (3%)
S.N.O.P_1	1/28/88 (7)	3.50	1.40 (4%)
	1/29/88 (8)	3.08	1.30 (4%)
	1/30/88 (9)	2.92	0.80 (3%)
S.N_1O.P_1	1/31/88 (10)	2.54	0.80 (3%)
	2/1/88 (11)	2.39	0.36 (2%)
	2/2/88 (12)	2.02	0.39 (2%)

The results of the hydraulic conductivity experiments run with hydrogen peroxide as the oxidant are shown in Figures 3-11 through 3-14. The experiment represented by Figure 3-11 was run on Permeameter Board #4 and by Figure 3-13 was run on Permeameter Board #2. Again the experiments had to switch perm boards because of the additional

breakthrough experiments.

In Figure 3-11, hydraulic conductivity decreased by 57% but showed an unparalleledd increase above 10^{-3} cm/s for five days. After a 53% initial increase, hydraulic conductivity remained almost constant, within 4%, for the first week. It then dropped off slightly and remained relatively constant, within 18%, until day 12. The three changes in permeant resulted in two decreases in hydraulic conductivity and the last one increased.

Intermittent flow conditions were responsible for data that produced Figure 3-12. For days 2 through 10 an average of two pore volumes was used to obtain the hydraulic conductivity data presented in Figure 3-11. However as the hydraulic conductivity continued to

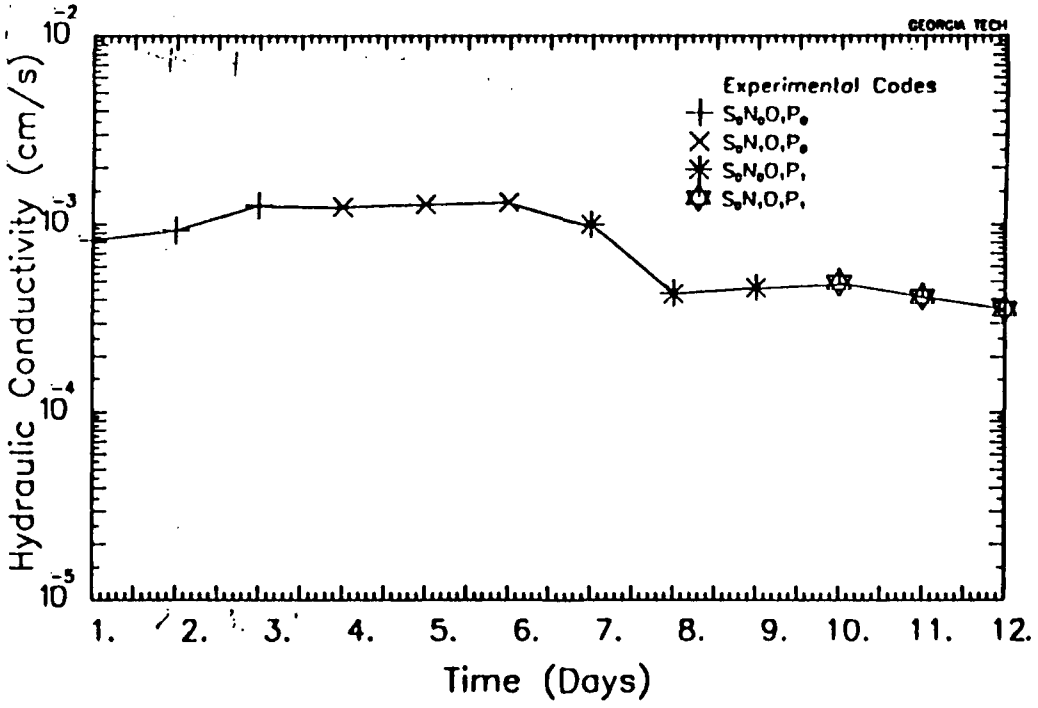


Figure 3-11: Hydraulic Conductivity vs Time (Without Microbial Seed and Hydrogen Peroxide As A Constant On Perm Bd #4)

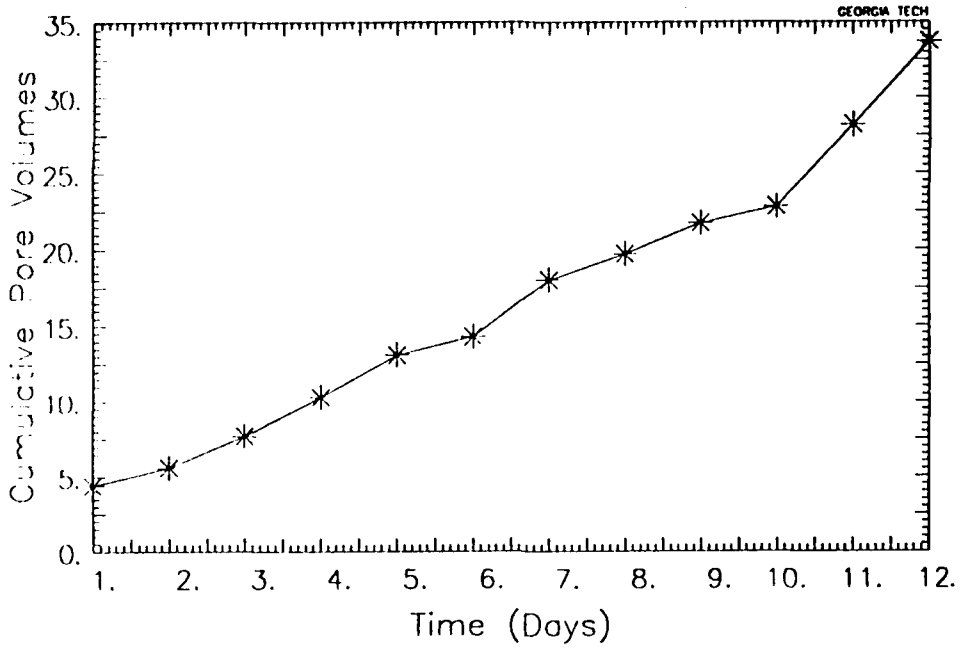


Figure 3-12: Permeant Flow in Pore Volumes Corresponding to the Experiment in Figure 3-11

maintain its relatively high value, more samples were taken on days 11 and 12. This accounts for the increase to over five pore volumes passed through the sample on these days. The pore volume of the soil sample used in the hydrogen peroxide experiment was *78.1 mL*, and *2632.3 mL* of permeant passed through it.

Table 3-6 contains the values for the data points and the standard

Table 3-6: Standard Deviations for All Data Points Contained in Figures 3-11

Experiment Code	Date of HC Run (Day)	K_{avg} (cm/s x 10^{-4})	S_K (cm/s x 10^{-5})
S..N..O₁P₀	1/26/88 (1)	8.24	8.72 (10%)
	1/27/88 (2)	9.28	12.6 (14%)
	1/28/88 (3)	12.6	9.21 (7%)
S..N₁O₁P₀	1/29/88 (4)	12.4	14.3 (11%)
	1/30/88 (5)	12.8	3.71 (3%)
	1/31/88 (6)	13.1	7.62 (6%)
S..N..O₁P₁	2/1/88 (7)	10.0	3.10 (3%)
	2/2/88 (8)	4.32	0.86 (2%)
	2/3/88 (9)	4.62	2.18 (5%)
S..N₁O₁P₁	2/4/88 (10)	4.93	3.37 (7%)
	2/5/88 (11)	4.15	2.88 (7%)
	2/6/88 (12)	3.56	1.62 (4%)

deviations of the data contained in Figure 3-11.

The second hydrogen peroxide experiment contained microbial life in the soil sample. Nutrients and pollutant were added on days 4 and 7 respectively. In Figure 3-12, hydraulic conductivity decreased by 94% with a somewhat erratic path over the first seven days of the experiment. Days 2 and 3 showed a sharp downward trend in hydraulic conductivity, decreasing 76%, followed by two days of increase, a day of

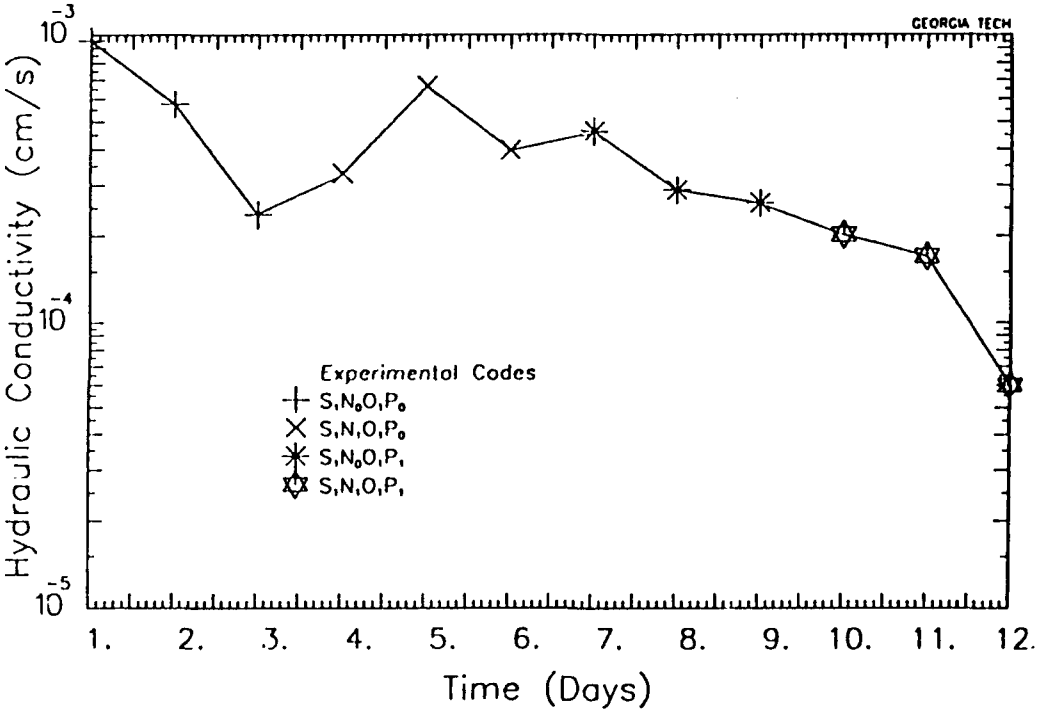


Figure 3-13: Hydraulic Conductivity vs Time (With Microbial Seed and Hydrogen Peroxide As A Constant On Perm Bd #2)

decrease, and a small increase with the permeant change. The last five days of the experiment showed a downward trend in hydraulic conductivity values. The three changes in permeant resulted in two increases in hydraulic conductivity and the last one decreased.

Continuous flow conditions were responsible for data that produced

Figure 3-14. This resulted in a large difference in pore volumes passed for the two hydrogen peroxide experiments. The rate changes of permeant passed through the sample did not correlate well with the changes in hydraulic conductivity. For instance, in Figure 3-14, a declining rate of pore volumes passed is shown for days 2 through 6. Even though the hydraulic conductivity (see Figure 3-13) is varying from a low of 2.37 x 10^{-4} cm/s to a high of 6.66 x 10^{-4} cm/s during this period, the amount of fluid passed through the sample each day was declining. The

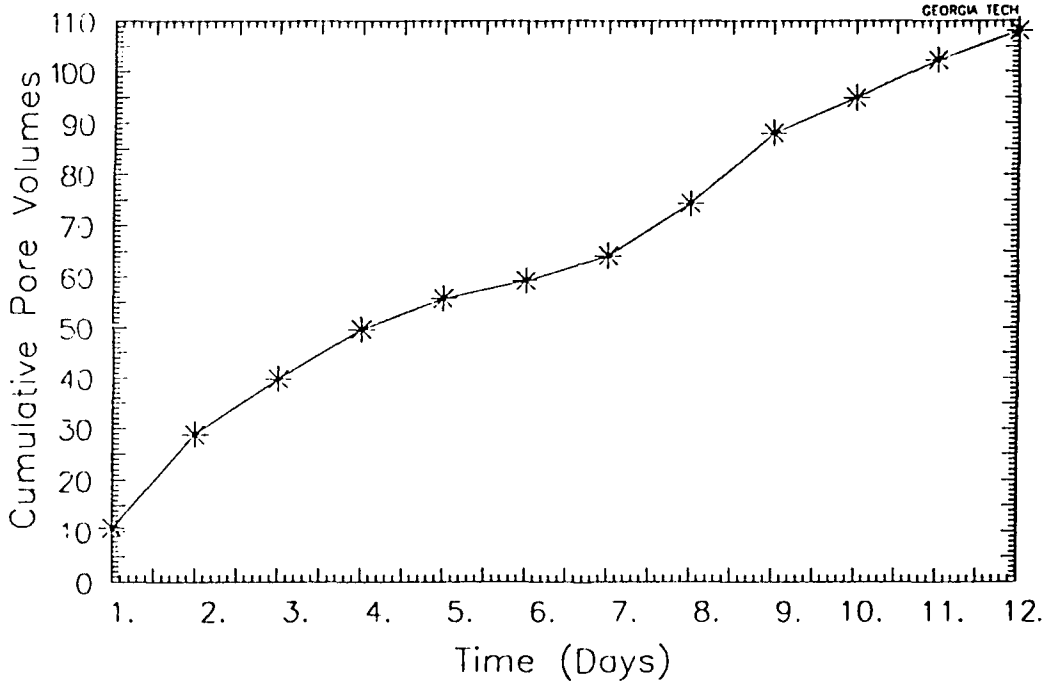


Figure 3-14: Permeant Flow in Pore Volumes Corresponding to the Experiment in Figure 3-13

remainder of the experiment showed either an increasing or constant rate of permeant flow and the hydraulic conductivity was declining. The pore volume of the soil sample used in this hydrogen peroxide experiment was 62.7 mL, and 6779.7 mL of permeant passed through it.

Table 3-7: Standard Deviations for All Data Points Contained in Figures 3-13

Experiment Code	Date of HC Run (Day)	K_{avg} (cm/s x 10^{-4})	S_K (cm/s x 10^{-5})
$S_1N_1O_1P_1$	2/17/88 (1)	9.77	6.47 (7%)
	2/18/88 (2)	5.77	2.82 (5%)
	2/19/88 (3)	2.37	0.76 (3%)
$S_1N_1O_1P_0$	2/20/88 (4)	3.31	1.26 (4%)
	2/21/88 (5)	6.66	4.66 (7%)
	2/22/88 (6)	3.99	1.59 (4%)
$S_1N_1O_1P_1$	2/23/88 (7)	4.63	2.24 (5%)
	2/24/88 (8)	2.89	1.83 (6%)
	2/25/88 (9)	2.60	0.96 (4%)
$S_1N_1O_1P_1$	2/26/88 (10)	2.02	0.60 (3%)
	2/27/88 (11)	1.70	0.48 (3%)
	2/28/88 (12)	0.60	0.28 (5%)

Table 3-7 contains the values for the data points and the standard deviations of the data contained in Figure 3-13.

One more hydraulic conductivity experiment was conducted as a control where the permeant was not altered. Results of this control

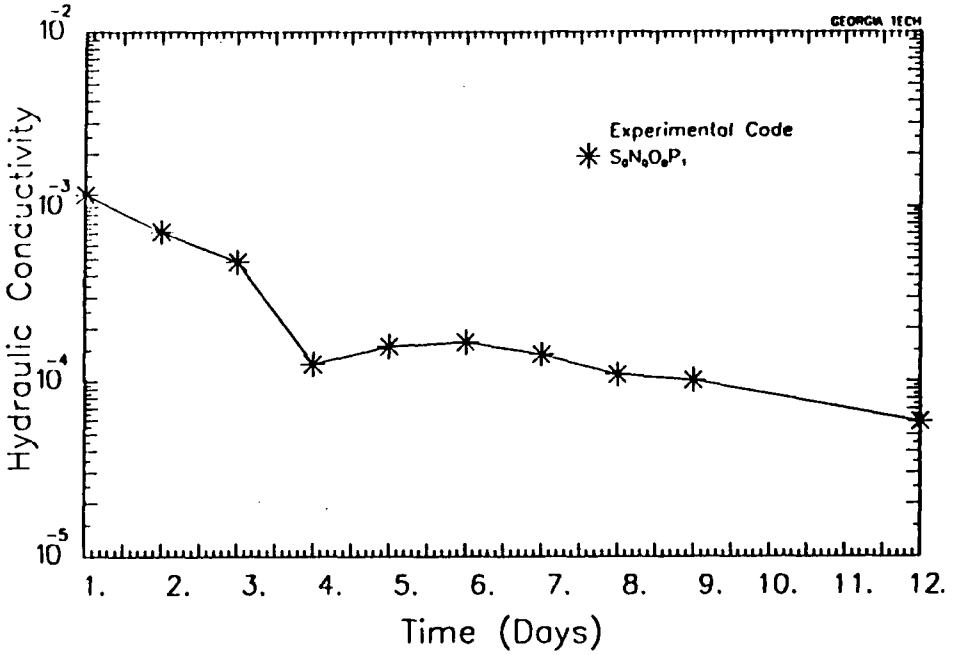


Figure 3-15: Hydraulic Conductivity vs Time (Without Microbial Seed and No Oxidant As A Constant On Perm Bd #4)

experiment were no different than any other hydraulic conductivity experiment. Hydraulic conductivity data shown in Figure 3-15 decreased by 89% for the first four days and then only decreased 6% for the remainder of the test.

Adsorption_Breakthrough_Curve

Two experiments were run to provide information concerning adsorption of 2,4-dichlorophenol onto soil particles. These experiments provided information concerning the length of time required to saturate the soil sample with pollutant. This in turn was meant to aid in distinguishing between adsorption and microbial degradation.

The permeant was 100 mg of 2,4-dichlorophenol dissolved in one liter of deaired tap water. The water was deaired by bubbling nitrogen gas through it until the dissloved oxygen concentration reached <0.2

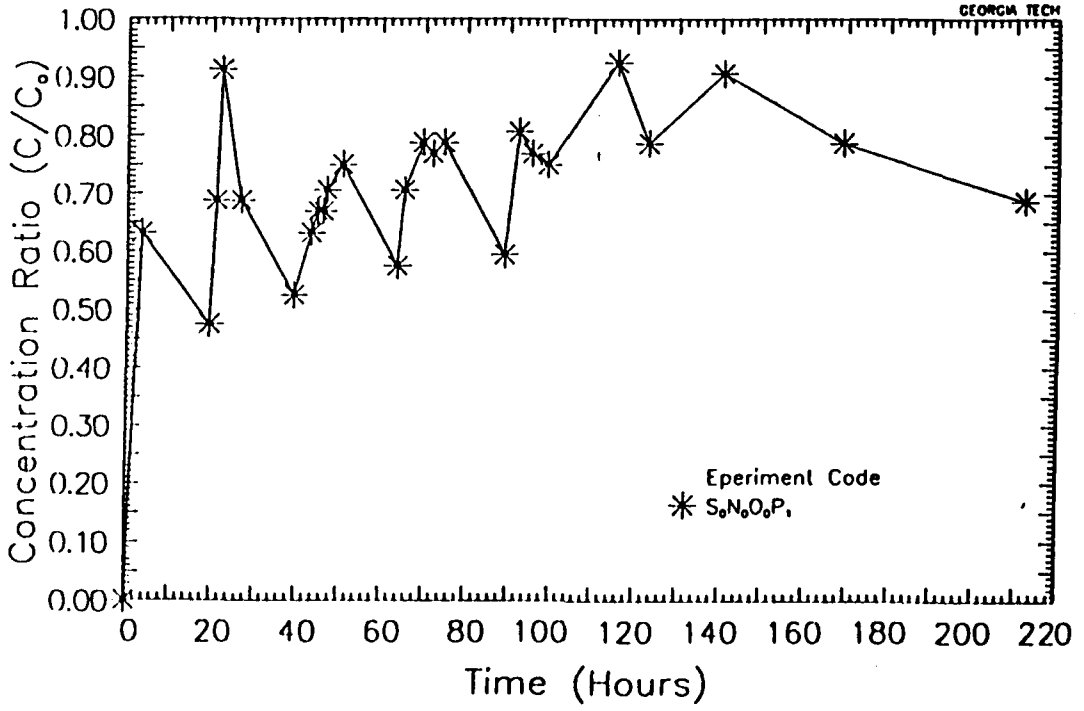


Figure 3-16: Breakthrough Curve #1 (Perm Bd #4)

mg/L. No nutrients were in the permeant.

Results of the first adsorption breakthrough test, which lasted 216 hours, are shown in Figure 3-16. No lag phase developed because the sample was back pressure saturated with the permeant. Ideally the sample should start off clean, free of pollutant, so there can be an initial concentration of zero in the soil sample. By back pressure saturating with the pollutant, the sample contained pollutant when the breakthrough experiment started.

Fluctuations in the breakthrough curve (see Fig. 3-16) were the result of intermittent flow conditions that existed at the beginning of the experiment runs. Flow was allowed during daylight hours and then closed off at night so the nitrogen supply would not be exhausted. The high points of the peaks represent the last sample taken during each day just before the system was shut off. The low points are the first sample points taken each morning after the system had been under stop flow conditions. Overnight the soil sample would adsorb 2,4-dichlorophenol under stop flow conditions. When flow was started the next morning the effluent concentration was lower until several pore volumes had passed through. The effluent concentration would then increase again. Increasing peak values indicated the sample was becoming increasingly more saturated each day. The decrease at the end was due to the hydraulic conductivity dropping so low that any measurable flow in a reasonable amount of time (5 hours) was impossible. The experiment was terminated at this point, and another adsorption breakthrough test was initiated so it could be run under continuous flow

conditions.

A second adsorption breakthrough test was run with the influent concentration, C_o, being 28 mg/L. C_o was decreased so it more closely matched the 2,4-dichlorophenol concentration used in the hydraulic conductivity experiments. The sample was back pressure saturated with deaired tap water and then the 2,4-dichlorophenol solution was placed into the influent reservoir. A long lag phase did not develop. Flow initially was very high, and permeant flowed easily through the soil sample. Continuous flow conditions were used for this experiment. The 2,4-dichlorophenol concentration in the effluent increased to 75% of the influent concentration in less than eight hours. The decrease in the C/C_o ratio which can be seen around the two day point occurred when the hydraulic head was only sustaining a minimal flow. After three days,

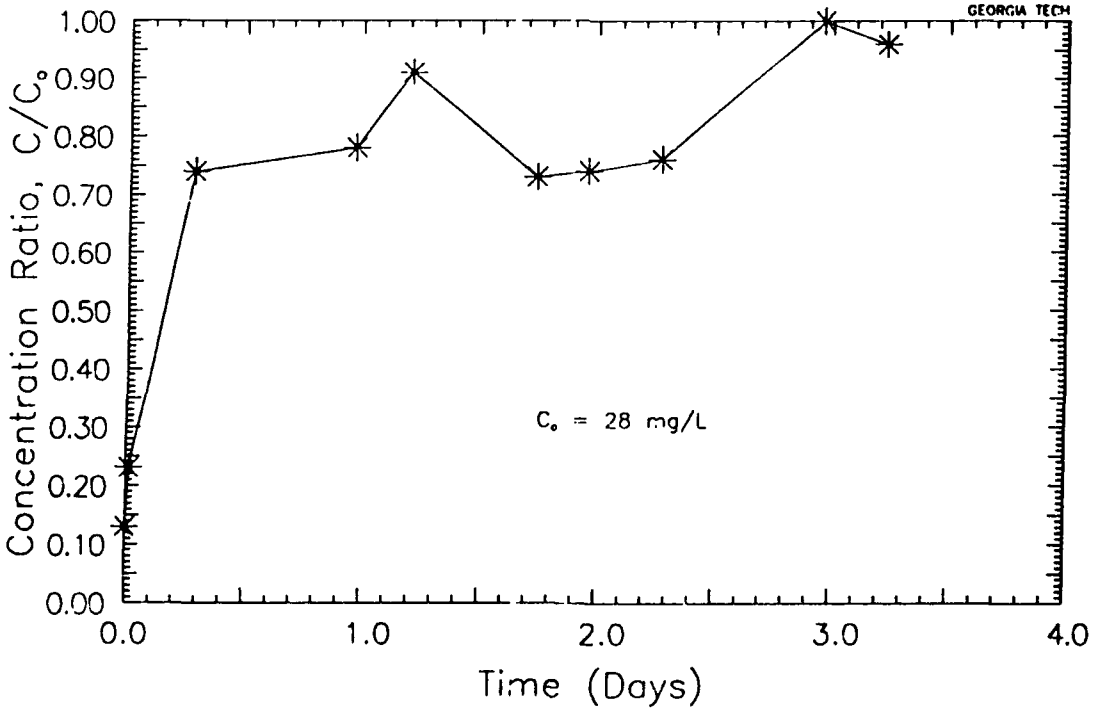


Figure 3-17: Breakthrough Curve #2 (Perm Bd #4)

effluent concentration equaled influent concentration. Results of the second adsorption breakthrough experiment are shown in Figure 3-17.

Adsorption Isotherm

Two isotherm experiments were performed as another effort to distinguish between microbial decay of the 2,4-dichlorophenol versus adsorptive attenuation. Both experiments involved the use of 25 bottles that were filled with various combinations of Ottawa sand, kaolinite clay, and a 2,4-dichlorophenol solution. All bottles were mixed thoroughly for ten hours.

The first isotherm experiment involved a mix of Ottawa sand and kaolinite clay. The total mass of sand and clay in each bottle ranged between 5 grams and 100 grams. The clay fraction in each bottle remained constant and matched that of the soil samples tested in the triaxial permeability devices, 3.4%. Of the 25 bottles, two were left void of sand and clay and only contained the 2,4-dichlorophenol solution at 45 mg/L. After being shaken for ten hours, the samples were allowed to sit for ten minutes, until the clay settled out and left a clear supernatant.

Once the clay had settled out, the supernatant was then filtered through 0.45 μm filter. Samples of the filtered blanks and unfiltered blanks were kept as a control on the UV analysis process. Filtered samples and unfiltered blanks were stored in a refrigerator until they could be analyzed for 2,4-dichlorophenol.

The analysis of the samples from the first isotherm test

unfortunately generated more questions than it answered. The unfiltered stock solution that represented what went into all 25 bottles yielded consistent results of 45.1 mg/L as read off of the calibration curve (see Fig. 2-9). The filtered stock solution however yielded results of 43.1 mg/L and 50.1 mg/L. The filtered samples taken from the bottles showed concentrations ranging between 35.3 mg/L and 49.0 mg/L. Four times the analysis showed a concentration greater than that of the stock put into the bottles initially. These four points were discarded because they had no meaning when attempting to determine the amount of 2,4-DCP that went from solution onto the solid. There were so many problems with the first isotherm run that another attempt was made.

It was assumed that the sand would not contribute in a significant way to adsorption, and the adsorption would take place on the surface of the clay. In the first adsorption experiment the larger weights of sand and clay proved to be too difficult to mix thoroughly. The second attempt involved only the use of kaolinite clay. The mass of clay used ranged from 5 grams to 20 grams.

In order to provide more control for the second attempt, the bottles contained only a 34 mg/L 2,4-dichlorophenol solution. The concentration was decreased because any small reduction in concentration would be more easily distinguished with 34 mg/L than with 45 mg/L. The analysis of the unfiltered stock solution showed a concentration of 34.1 mg/L as read off the same calibration curve used previously. Fortunately none of the filtered samples or the stock solution samples exceeded the 34.1 mg/L stock concentration.

After the UV-spectroanalysis data was gathered from both isotherm attempts, the amount deposited on the soil particle was calculated. This was done by taking the difference between the initial concentration and the final concentration then multiplied by the volume placed in the bottle.

$$(C_i - C)V \qquad 3\text{-}1$$

The mass deposited on the soil particle, X, was then divided by the mass of the soil, M. This produced an X/M ratio. The X/M values were placed in two models commonly associated with adsorption isotherms, the Freundlich and Langmuir models.

The experimental values for X/M and C_{eq} were substituted into the Freundlich and Langmuir models. The results are shown in Figures 3-18 and 3-19. The data from both isotherm experiments are plotted on each

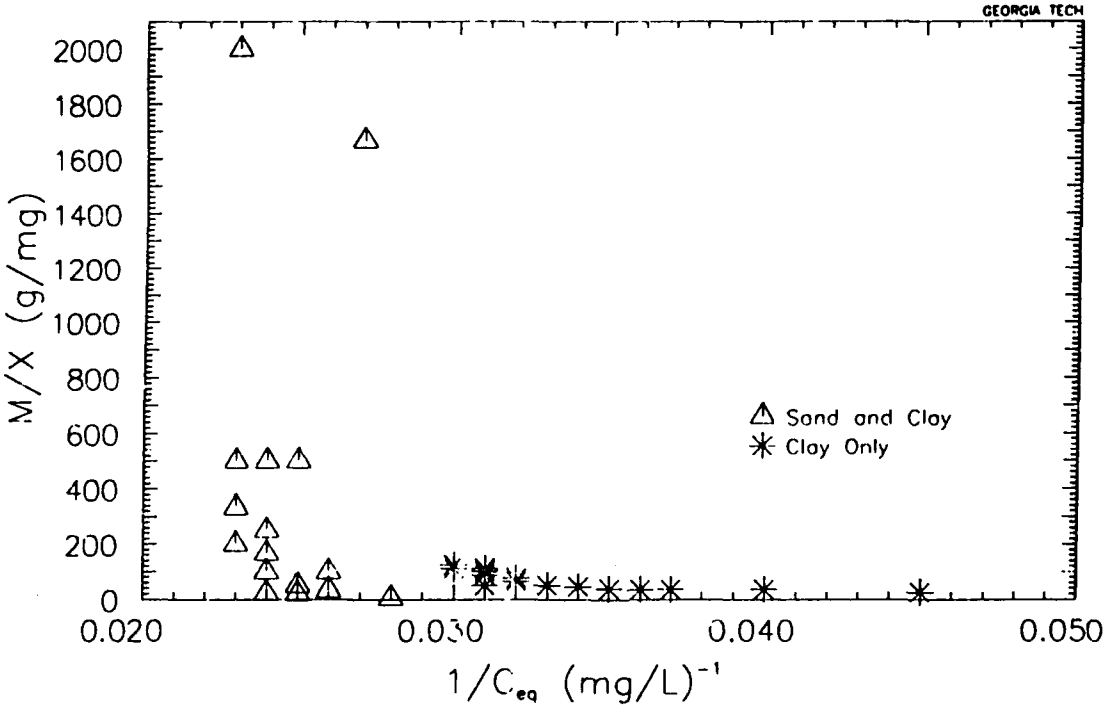


Figure 3-18: Experimental Data Langmuir Plot

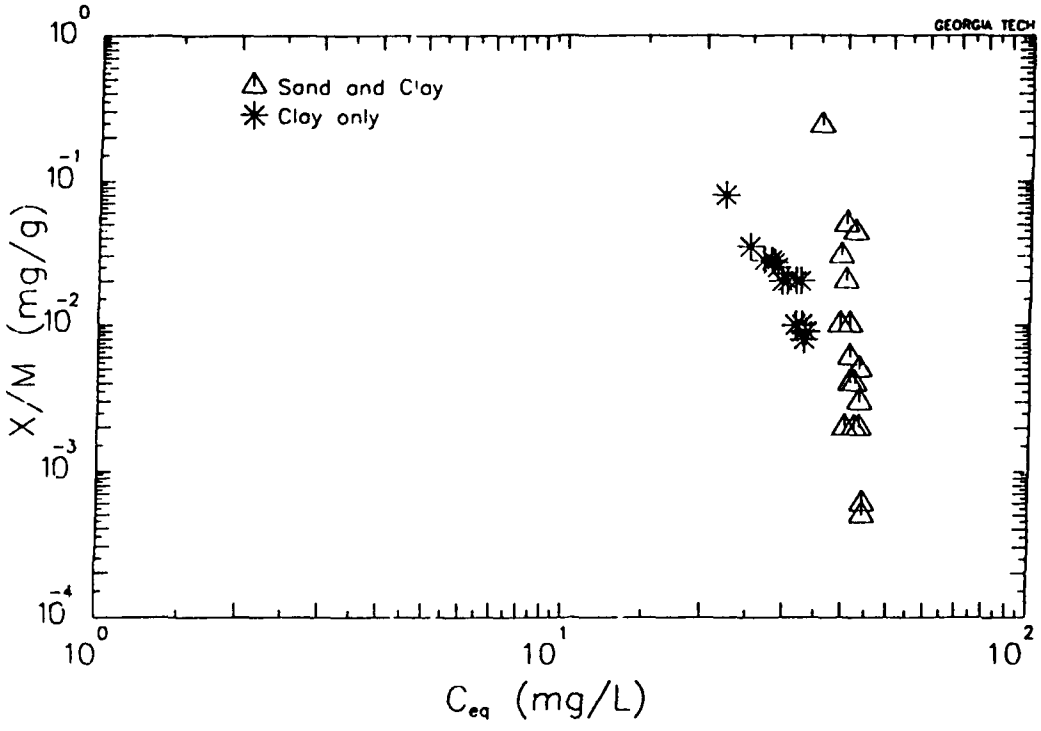


Figure 3-19: Experimental Data Freundlich Plot

graph. A normal isotherm plot slopes up and to the right. These experimental plots at best were almost vertical and at worst sloped down and to the right.

Microbial Degradation

In determining attenuation of 2,4-dichlorophenol in the soil samples, the effect of microbes in the soil sample was studied. As mentioned in Chapter 2, the microbes were grown on 2,4-dichlorophenol in the laboratory. Microbial seed was obtained from a local wastewater treatment plant. The microbes were then mixed into the soil sample and the experiment started. These experiments were the same experiments spoken of earlier in the hydraulic conductivity section. The attempt to see microbial degradation ran concurrently with the measurement of hydraulic conductivity.

When placed into the soil sample, the microbes went through a change in environment. The microbes had been in the biological reactor

with a constant 2,4-dichlorophenol, nutrient, and oxygen supply. Once in a sample the microbes would lose two, possibly all three of these, for at least three days as the experiment progressed. On the seventh day the microbes would be provided 2,4-dicholorophenol but not nutrients. On the tenth day, except for the experiment with no oxidant, the microbes had all they needed to flourish, nutrients, oxygen and a carbon source.

How the soil samples from the oxygen, hydrogen peroxide, and no oxidant experiments reacted to a 30 mg/L concentration of 2,4-dichlorophenol is shown in Figures 3-20 through 3-22. A concentration of 30 mg/L was used because the data from the biological reactor showed that volatility was 42%, and the microbes were having a difficult time surviving at 100 mg/L (2,4-dichlorophenol). Total suspended solids in the reactor was 421.3 mg/L, and the volatile suspended solids was 177.7 mg/L.

The time scale in the figures is elapsed time, starting from day 7 of the hydraulic conductivity experiments. Effluent samples were not taken until the seventh day of the experiment, the day 2,4-dichlorophenol was first introduced.

Perm board #1 shown in Figure 3-20 had the greatest attentuation during the nine day period samples were taken. This sample had molecular oxygen as its oxidant. The initial DO of any new permeant stock was between 7.0 and 8.0 mg/L. The DO of the effluent samples was often 5.0 mg/L or less. As might be expected, the initial sample had a low 2,4-DCP concentration, but the concentration increased to 22 mg/L

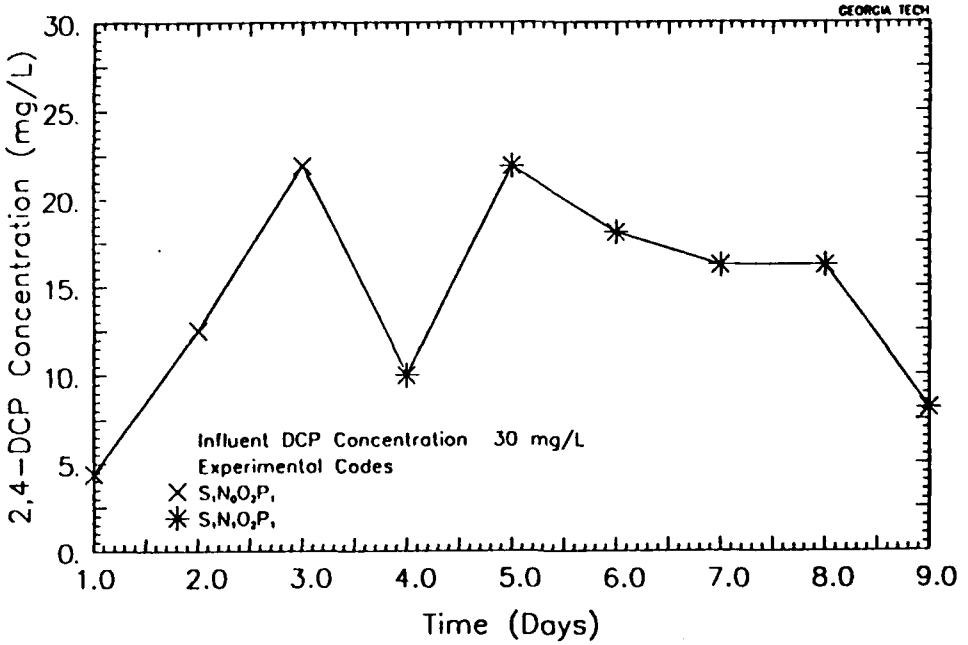


Figure 3-20: Pollutant Concentration vs Time (Perm Bd #1)

before falling to less than 10 mg/L. The concentration then increased again to 22 mg/L. After a second day of nutrients being in the sample, the effluent concentration fell steadily to 10.5 mg/L. After providing all the microbes needed, nutrients, oxidant and a carbon source, the effluent concentration of 2,4-dichlorophenol decreased.

Experimental results from perm board #2 are shown in Figure 3-21. Hydrogen peroxide was the oxidant in this system. Effluent concentration increased after a small decrease on day 2. There was however another decrease by day 6. The initial DO concentration was 0.7 mg/L or less for any stock solution. The initial stock concentration of hydrogen peroxide was 9 mg/L.

Experimental results from perm board #3 shown in Figure 3-22 showed an initial effluent concentration of 8 mg/L 2,4-dichlorophenol, but then increased to 22 mg/L by the end of the ninth day. After the 4-day point and addition of nutrients, the concentration decreased from 13.5 mg/L to 10.0 mg/L. This system was oxidant limited, and initial DO the

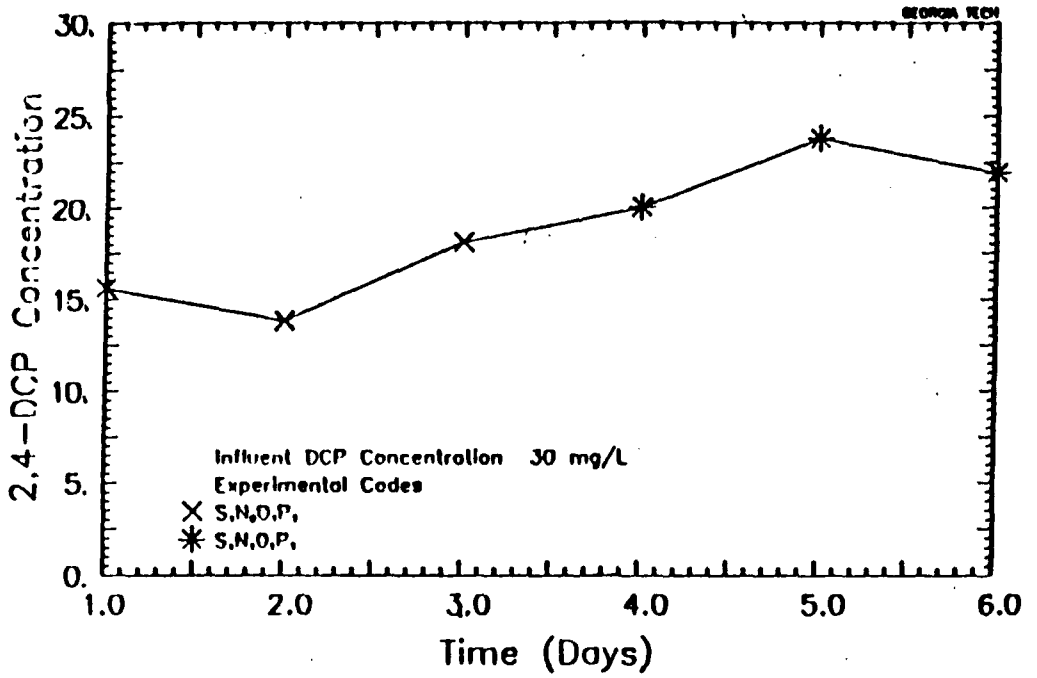


Figure 3-21: Pollutant Concentration vs Time (Perm Bd #2)

concentration of any stock solution was 0.9 mg/L or less. This experiment was also allowed to run for nine days because the hydraulic conductivity never decreased so much that the flow was severely limited.

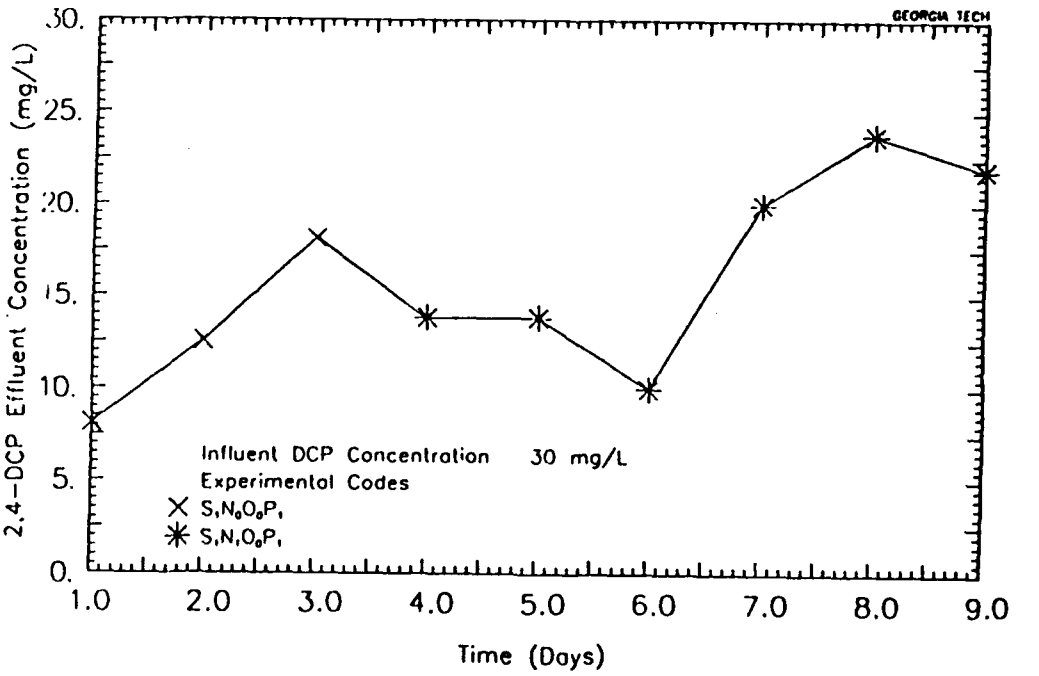


Figure 3-22: Pollutant Concentration vs Time (Perm Bd #3)

CHAPTER 4
Conclusions

Four triaxial permeability devices provided an opportunity to reproduce underground forces and an environment where microorganisms could live. With the triaxial permeability devices, effects of different permeants can be studied in detail without a danger of contaminating an aquifer with an experimental remediation method; conditions within an aquifer, temperature, pH, effective stress, porosity, hydraulic conductivity, and pore water can be reproduced within the laboratory.

The triaxial permeability devices were constructed, tested, and operated according to design. When systems had to be redesigned to allow for continuous flow, this was done also. Solving the problem of intermittent operation demonstrated flexibility. Future adaptations of the triaxial permeability devices to meet changing research needs will be just as easily made.

The first conclusion that can be made at this early point is hydraulic conductivity decreased over the short twelve or fifteen day period these tests were run. Eight experiments produced hydraulic conductivity data. In all eight, k values ultimately decreased anywhere from 36% to 97% of their original values. A similar result was discovered by researchers carrying out experiments with an aquifer at Kelly AFB, Texas.[22,23] A decrease in hydraulic conductivity with the passage of permeant was recorded in laboratory soil samples. Their results can be seen in Figure 1-17.

The decrease in hydraulic conductivity as seen by Kelly AFB engineers was also an erratic and unpredictable event. With the passage of permeant through the sample, as with the passage of time in this research, a prediction of the next hydraulic conductivity value was difficult to make. The second conclusion from this research was, even with a change in permeant, a prediction of the next hydraulic conductivity value could be made only with limited certainty. Seven of the eight experiments where hydraulic conductivity values were recorded involved permeant changes. In all the permeant was changed 21 times. Out of these 21 changes, hydraulic conductivity decreased a dozen times, increased eight times, and remained constant once.

Even though hydraulic conductivity ultimately went down in all cases, the rate of fluid flow did not always accurately reflect the change in hydraulic conductivity values. In some instances during continuous flow experiments, the rate of fluid flow would appear to be decreasing as hydraulic conductivity was increasing. This can possibly be explained by the fact that flow was a continuous occurance and the measuring of hydraulic conductivity was a relatively short lived event. Flow and hydraulic conductivity would have to be measured simultaneously under continuous flow conditions to achieve a closer correlation.

The ability of a soil sample to adsorb 2,4-dichlorophenol was shown to a small degree. The two breakthrough curve experiments provided valuable results. The first experiment, though never reaching 100% saturation, provided information concerning the effects of intermittent flow on effluent concentration. Intermittent flow produced a daily

peaking effect (see Figure 3-16) as the effluent 2,4-dichlorophenol concentration increased when flow was allowed during the day and decreased after being under stop flow conditions overnight. Therefore the importance of continuous flow was seen and was employed for the second breakthrough curve. It was shown in the second experiment that a soil sample could adsorb 2,4-dichlorophenol to the point of saturation.

Another important conclusion from the breakthrough curve experiments was a soil sample must be back pressure saturated with a clean permeant. Samples must start clean in order to accurately assess the amount of time it takes to become satuarated with a pollutant .

The two isotherms provided less conclusive evidence for adsorptive capability than the breakthrough experiments. One possible explanation for the results shown in Figures 3-18 and 3-19 was a system that had almost no adsorptive capability; there was one good data point and all others were experimental scatter. Without further investigation, a more definite explanation is not possible at this time. However, adsorptive attentuation is a factor that must be considered in any underground remediation proposal. The ability to predict the location and movement of an underground pollutant plume can be dramatically affected by adsorptive retardation. Mehran, *et al.*,[28] developed an expression that quantifies the relationship between pore water velocity and pollutant velocity in an aquifer. This is shown in Equation 1-4.

Microbial attenuation was studied in conjunction with changes in hydraulic conductivity. The last six or more days of each experimental series was devoted to studying the effect of microbes in the soil sample

on 2,4-dichlorophenol. Triaxial permeability device #1 showed a one time 50% disssolved oxygen reduction in the effluent. Also after the system became accustomed to the presence of nutrients, oxygen, and 2,4-dichlorophenol in plentiful quantities, a consistent decrease in effluent concentration was noted. Unfortunately this downward trend was not repeated in the other two systems used for microbial studies. Only inconsistent behavior was noted here with maybe a hint of an effluent decrease on the last day.

However, microbial degradation of 2,4-dichlorphenol and other organic chemicals is a documented fact and should be an alternative when ground-water clean up options are being considered. Lab and field examples can be shown that strongly indicate microbial degradation is taking place.

In the lab, Suflita and Miller[44] showed that 2,4-dichlorophenol could be degraded under anaerobic and aerobic conditions. They used genuine aquifer material in their experiments. Bouwer and McCarty[45] using 3-mm glass beads for their porous matrix showed a biological reduction in the concentration of 1 and 2 carbon aliphatic compounds. Their work was performed under methanogenic conditions. Vogel and McCarty[46] using 6-cm quartzite rocks along with Parsons, *et al.*,[47] and Wilson, *et al.*,[48] who used aquifer material defined a biotransformation mechanism, reductive dehalogenation, that could change PCE to vinyl chloride. Wilson, *et al.*,[48] and Majors, *et al.*,[49] also showed the potential for biological remediation of gasoline spills by working with BTX fractions. They both worked with genuine aquifer materials and

demonstrated that the biological decay of BTX fractions could take place in methanogenic and aerobic environments.

In the field, West Germans[47] cleaned an aquifer that contained significant quantities of both aliphatic and aromatic (BTX) compounds. Their primary reason for stating that *in-situ* biological means cleaned the aquifer was that only after addition of nitrates and nutrients did reductions in pollutant concentrations take place. Kelly AFB, Texas[48,49] is currently attempting *in-situ* biological remediation of an aquifer containing chlorobenzene and 1,1-dichloroethylene. They are attempting this in an aerobic environment using hydrogen peroxide as the O_2 source. Results for biological clean up are encouraging, but the aquifer soil type does not lend itself well to fluid transfer. Hydraulic conductivity was shown to decrease with time to the point where fluid flow became difficult (see Fig. 1-17).

Piotrowski[50] at a site in Montana has shown that *in-situ* reclamation could work on an aquifer containing PCP and creosote. Like at Kelly AFB[48,49], hydrogen peroxide was used as the oxidant. Three important results have come from Piotrowski's[50] work so far. First, creosote requires an oxic environment to be biologically degraded. Second, oxic conditions can be created in large sections of an aquifer. Finally, EPA has mandated for the first time use of *in-situ* techniques on a full scale basis.

In-situ biological reclamation is now moving toward legitimacy with the EPA approval for a full scale clean up in Montana. Lab work in this area will continue into the forseeable future, and this lab work will be

spurred on by more successful applications in the field. Given correct conditions and adequate study *in-situ* biological reclamation of contaminated ground water will prove to be an effective treatment method.

APPENDIX

TRIAXIAL PERMEABILITY DEVICE
OWNER'S MANUAL

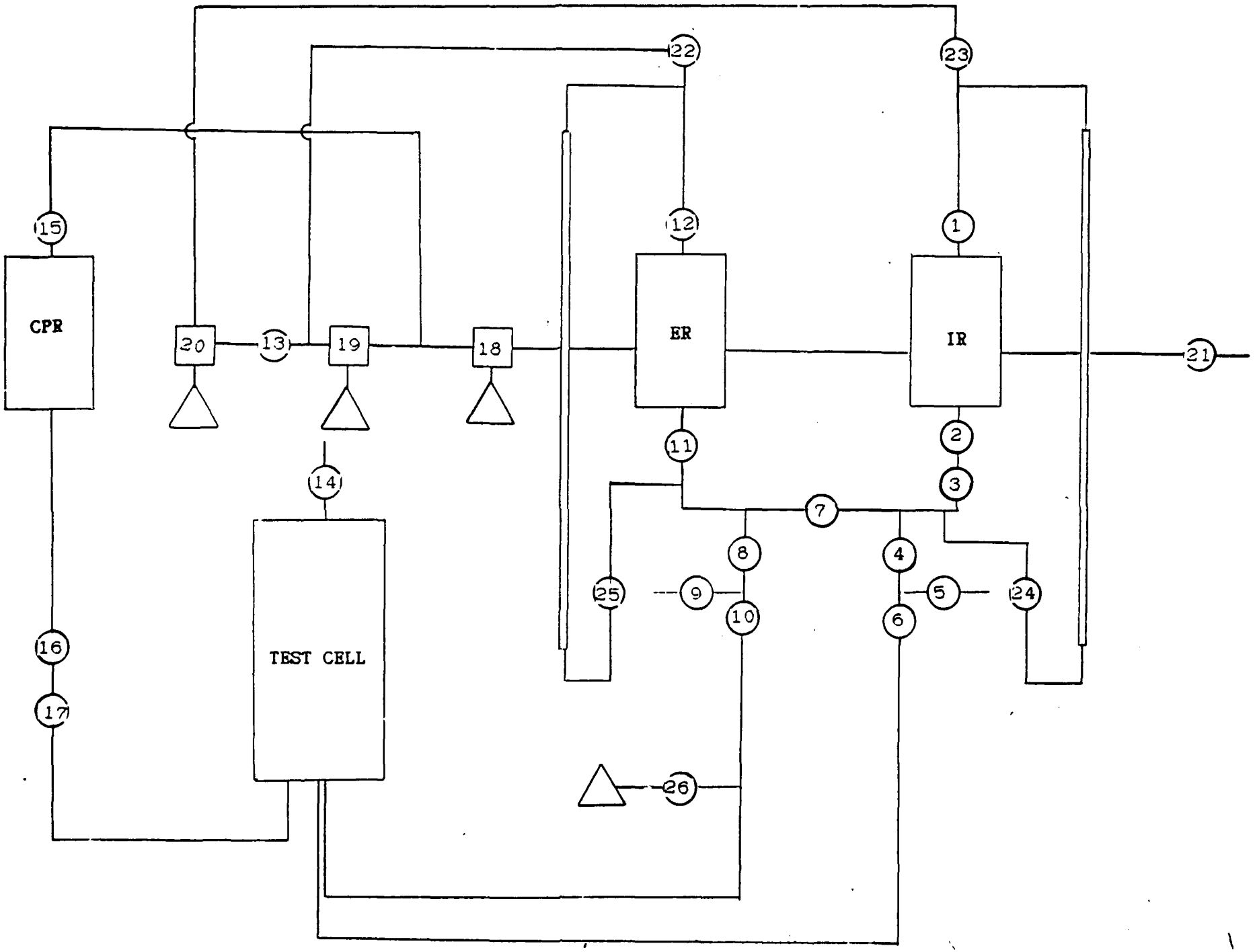


Figure A-1: Valve Numbering Scheme

APPENDIX A-1

SAMPLE PREPARATION

1. Weigh to within ±0.1 g a sample of soil.

2. If clay or silt present in sample place a piece of filter paper on top of the #200 sieve screen (if testing a soil with a large amount, >10%, of fines use the porous stones instead of the sieve screen) and place onto the bottom platen.

3. Fit two rubber O-rings onto bottom of membrane stretcher and roll up to the middle.

4. Pass the rubber membrane through the membrane stretcher and wrap membrane over the ends of the stretcher.

5. Attach the membrane stretcher's hose to the vacuum pump. If there are no leaks the membrane will form a smooth surface on the inside of the membrane stretcher.

6. Put the membrane stretcher on the bottom platen. Be careful not to let the sieve screen and filter slip to the side.

7. Carefully pour soil into the membrane stretcher through a funnel from a constant height. Tap the side of the membrane stretcher in order to vibratory compact the soil sample.

8. Level the top of the sample carefully until it is flush with the top of the membrane stretcher.

9. Place the filter paper (if fines present) directly onto the soil and the the sieve or porous stone on top of the filter paper.

10. Roll the membrane off the membrane stretcher onto the bottom platen followed by the O-rings to seal the membrane in place. Keep the O-rings on the round part of the bottom platen.

11. Turn the vacuum pump off. The membrane will now cling to the sample.

12. Roll the membrane of the top of the stretcher and carefully slide the stretcher off of the sample.

13. Put the top platen on the sieve screen and carefully pull membrane up around platen. Roll two O-rings down onto the top platen and seal off the sample.

continued on next page

14. Attach the test cell effluent line to the top platen.

15. Carefully lift the sample and place into permeameter board.

16. Attach the effluent line (white plastic fitting) to the vacuum pump. This will draw the membrane tightly around the sample and make it stiff.

17. Obtain the average height and diameter of the sample.

18. Construct the test cell around the sample. The sample is now ready to be pressurized within the test cell. See Appendix A-2 for test cell procedures.

19. Once the test cell has been pressurized detach the effluent line from the vacuum pump and attach it to the permboard.

20. Begin back pressure saturation. See Appendix A-3 for back pressure saturation procedures.

APPENDIX A-2

TRIAXIAL CELL PREPARATION

1. After sample has been mounted (see sample prep section) the triaxial cell cylinder is placed in the bottom plate groove.

2. The top plate is fitted accordingly onto the cylinder. And the three threaded rods are placed in their corresponding holes.

3. The three nuts are screwed into place and tightened down. These three nuts must be tightened down very firmly or the triaxial cell will leak when pressurized.

4. The top bulkhead fitting is removed from the cell pressure reservoir. The cell pressure reservoir is completely filled with tap water. Valve #16 (see Fig A-1) is opened to allow water to flow part way down.

5. Valve #17 is opened and the triaxial cell begins to fill with confining fluid (water). Valve #14 must also be opened to allow air to bleed out of the triaxial cell. Fill the triaxial cell until the confining fluid level is approxiamately 2.5 cm from the top plate.

6. Close valve #17 and replace the top bulkhead fitting on the cell pressure reservoir. Screw valve #15 back into place.

7. Close valve #14 completely. The cell is now ready to be pressurized to the desired confininig stress.

APPENDIX A-3

BACK PRESSURE SATURATION

1. Close all valves and have 3-way valves #1 and #12 open to atmosphere. (For all these instructions see Figure A-1)

2. Turn on valve #21 (gas bottle or house air) and adjust Fairchild regulators to desired cell, back, and high pressures.

3. Turn 3-way valve #1 to gas feed and open pliug valves #15, #16, and #17 to pressurize test cell. Also open needle valves #22 and #23. This allows gas to flow to the top of the influent/effluent reservoirs and the influent/effluent site glasses.

4. Open plug valves #2, #4, #8, #11, and #26.

5. Open plug valve #3 and slowly open plug valve #10.

6. Very slowly open plug valve #6 part way. Permeant should begin to flow through the soil sample. Do not let the permeant flow too quickly through the sample because it could be damaged. Liquid will begin to appear in the effluent reservoir. Allow flow to continue like this for several minutes.

7. Close plug valves #3, #6, and #10.

8. Open 3-way valve #12 to gas feed.

9. Open needle valve #7 completely.

10. Open plug valves #6 and #10. Back pressure gauge and pore pressure gauge should read the same values. Record cell, back, and pore pressures. Allow this situation to go on for 5 minutes.

11. Close plug valves #6 and #10. Increase cell pressure by Δcp. Record cell pressure and after 3 minutes record pore pressure value.

12. Increase back pressure by an amount equal to Δcp.

13. Repeat steps 10, 11, and 12. Each time being sure to record the pore pressure and cell pressure values. Once the desired B-value (see discussion of B-value in Chapter 4)is reached, allow sample to consolidate over night at the desired effective stress level by closing plug valves #6, #10, and #17 to isolate the sample.

14. Close needle valve #7 completely before beginning hydraulic conductivity data collection.

APPENDIX A-4

HYDRAULIC CONDUCTIVITY MEASUREMENTS

1. Open plug valves #3, #24, and #25. This allows fluid to flow into the site glasses. The water in the site glasses should rise to the level of the water in the influent and effluent reservoirs. If the water doesn't go that high, then raise the reservoir up until the water flows in. Check to make sure all the proper valves are open.

2. To set the desired gradient (see discussion on gradient in Chapter 2) simply raise and/or lower the influent and effluent reservoir until the desired head difference is achieved. Record the fluid levels in the influent and effluent sight glasses. These readings are entered in the notebook as h_1 and h_3 respectively. See derivation of hydraulic conductivity equation in Chapter 2.

3. Plug valve #6 should be closed and plug valve #10 should be open.

4. The fluid flow will be flowing from influent sight glass to effluent sight glass. In order to do this, close plug valves #3 and #11. Now once the run begins the effluent sight glass level will rise as much as the influent sight glass level falls. Remember the derivation in Chapter 2 assumes outflow equals inflow.

5. Open plug valve #6 and simultaneously start the timer to begin the hydraulic conductivity run.

6. When the level in the influent sight glass has fallen the predetermined distance, stop the timer and quickly close plug valve #6.

7. Again record the levels of the influent and effluent sight glasses. Record thse in the notebook as h_2 and h_4 respectively.

8. Open plug valves #3 and #11 to allow the sight glass levels to return to their original positions.

9. Close plug valves #3 and #11.

10. Repeat steps 2-9 until consistant results are achieved or until two pore volumes have been passed through the sample.

APPENDIX A--5

SAMPLE TAKING

1. In order to take a sample, the most important thing to remember is only permeant that has flowed from the influent reservoir through the sample is what one wants. One does not want the permeant that was in the influent/effluent sight glasses nor the effluent reservoir.

2. Close plug valves #11, #24, and #25. This closes off the sight glasses and the effluent reservoir.

3. Very slowly open needle valve #9. While doing this do not let the pore pressure fall below 10 psi.

4. Allow whatever amount of permeant come out that one wants.

5. Close needle valves #9.

6. Open plug valves #11, #24, and #25, and return to normal flow patterns.

APPENDIX A-6

CONTINUOUS FLOW OPERATION

1. Close plug valves #6, #10, and #17. This isolates the sample.

2. Close plug valves #24 and #25. This takes the sight glasses out of the loop.

3. Turn 3-way valves #1 and #12 180°. So the gas feed will be coming from the bottle of gas.

4. Close the small needle valve on the nitrogen bottle regulator. The pressure gauges from the Fairchild regulators should begin to fall.

5. Open up the nitrogen gas bottle regulator completely by turning the large brass screw counterclockwise until it is loose. Do not let it fall on the floor.

6. As the Fairchild gauges get to about 10 psi, open the small needle valve on the nitrogen bottle regulator.

7. Take the large brass screw on the nitrogen bottle regulator and turn it clockwise until the pressure on the Fairchild cell pressure reads the desired back pressure.

8. Close the small needle valve again.

9. Unhook the nitrogen line from the cell pressure regulator and hook it up to the T connecting the effluent and influent reservoirs.

10. Open the small needle valve on the nitrogen bottle regulator.

11. Open plug valves #6 and #10. Flow should be restored and the pore pressure gauge will be reading the same pressure that is in the effluent reservoir.

APPENDIX B--1

TRIAXIAL PERMEABILITY DESIGN DRAWINGS

TRIAXIAL CELL

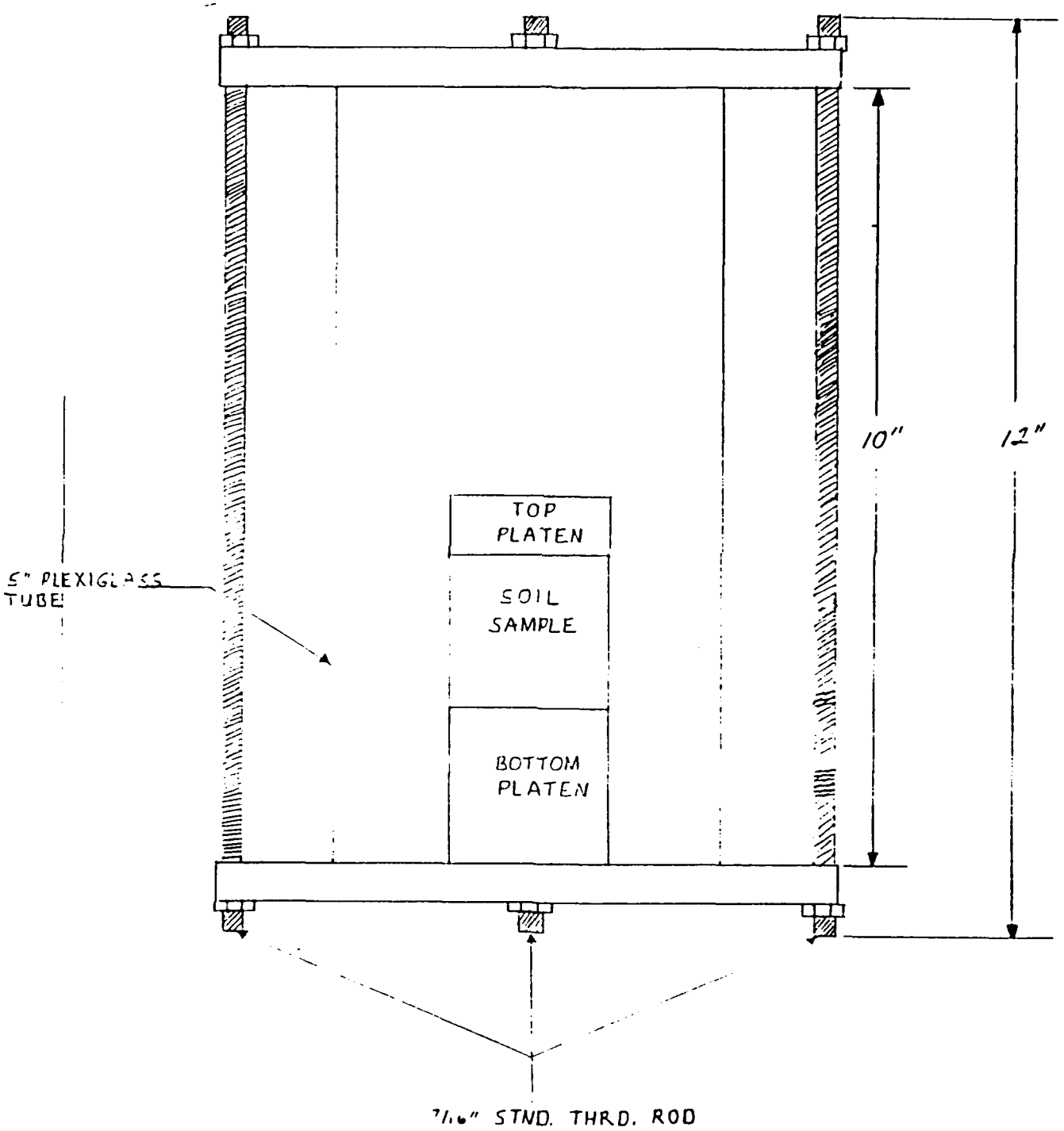


Figure B-1: Test Cell w/ Sample

INFLUENT/EFFLUENT RESERVOIR

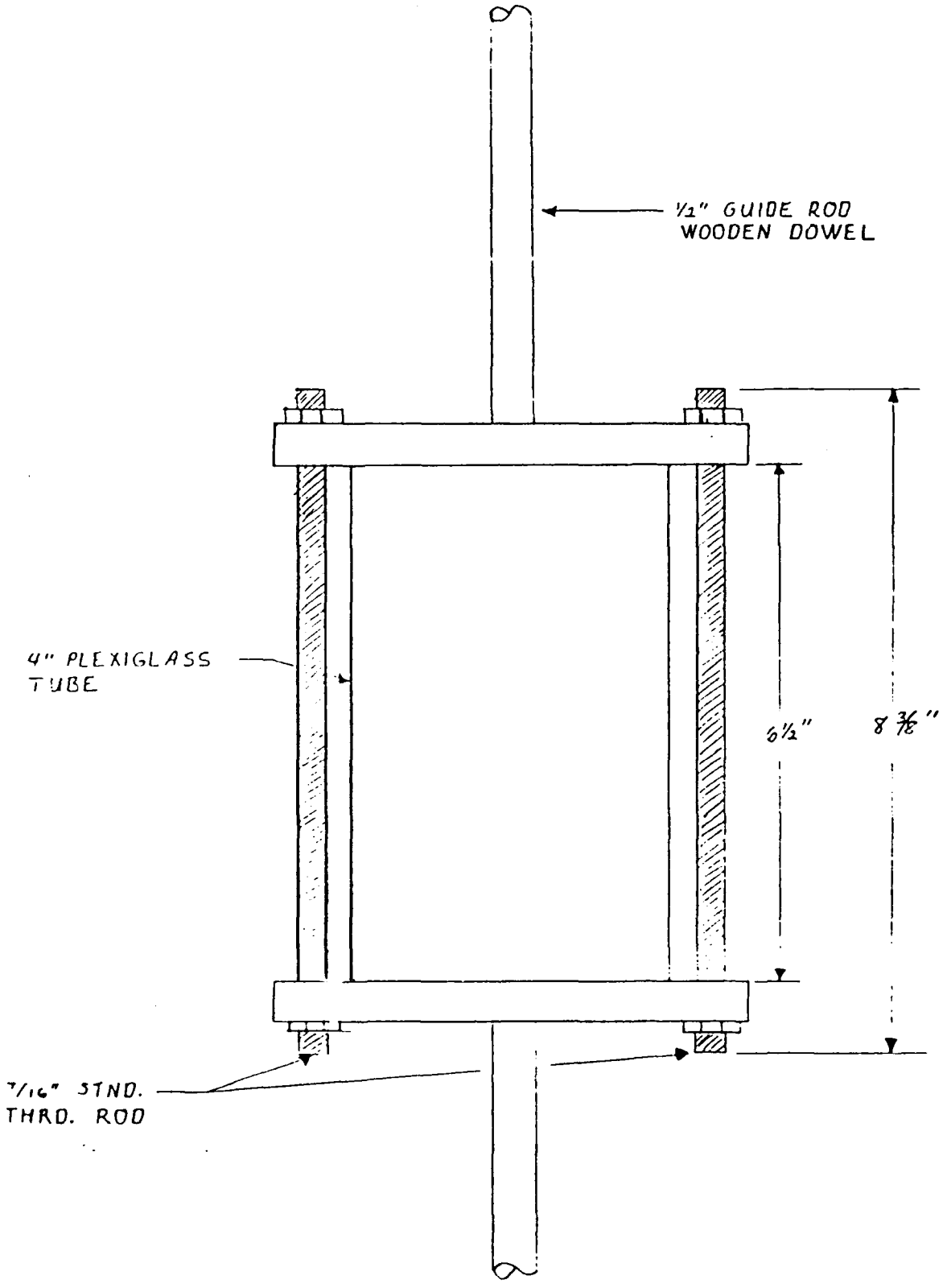


Figure B-2: Influent/Effluent Reservoir

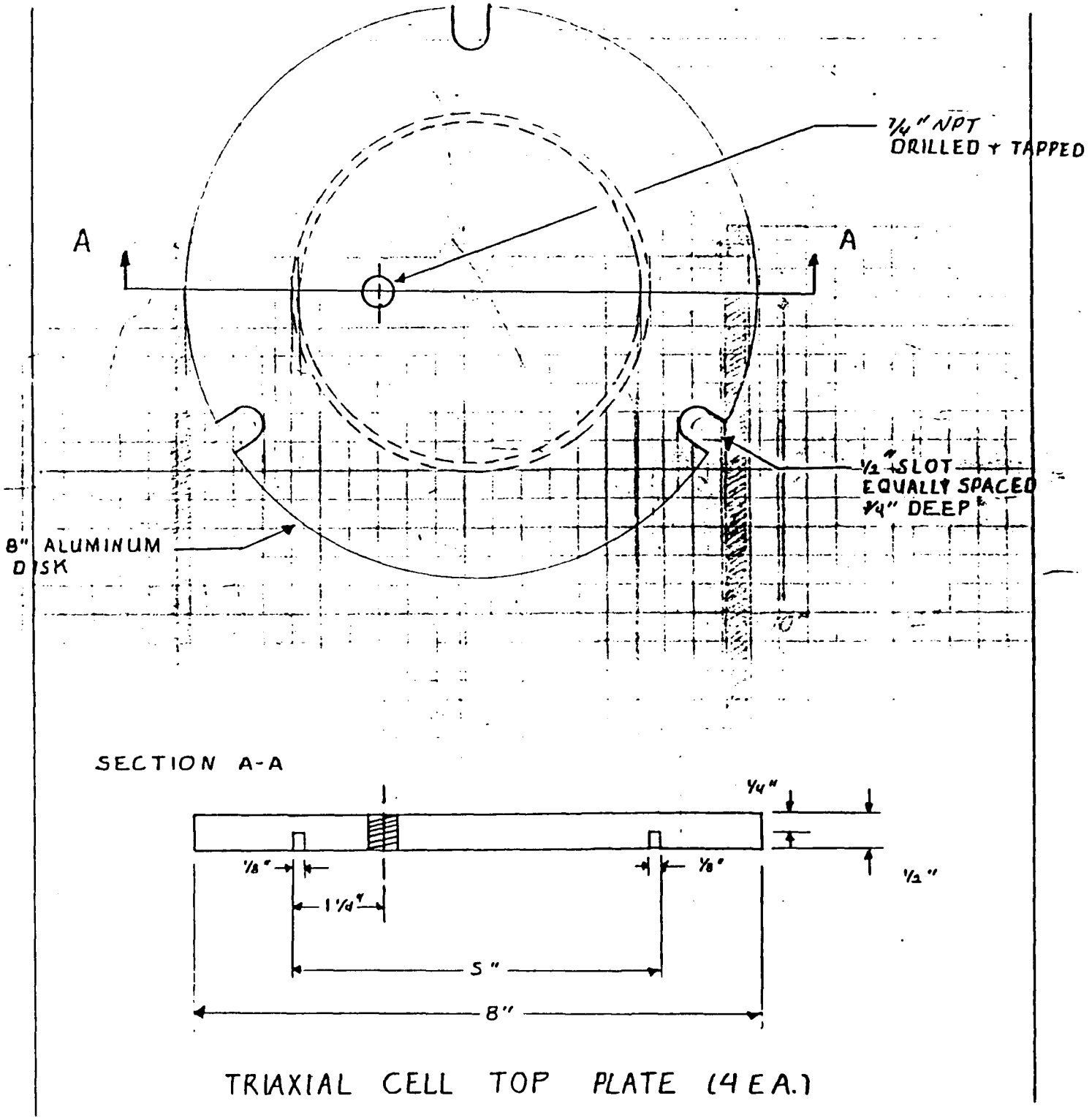


Figure B-3: Test Cell Top Plate

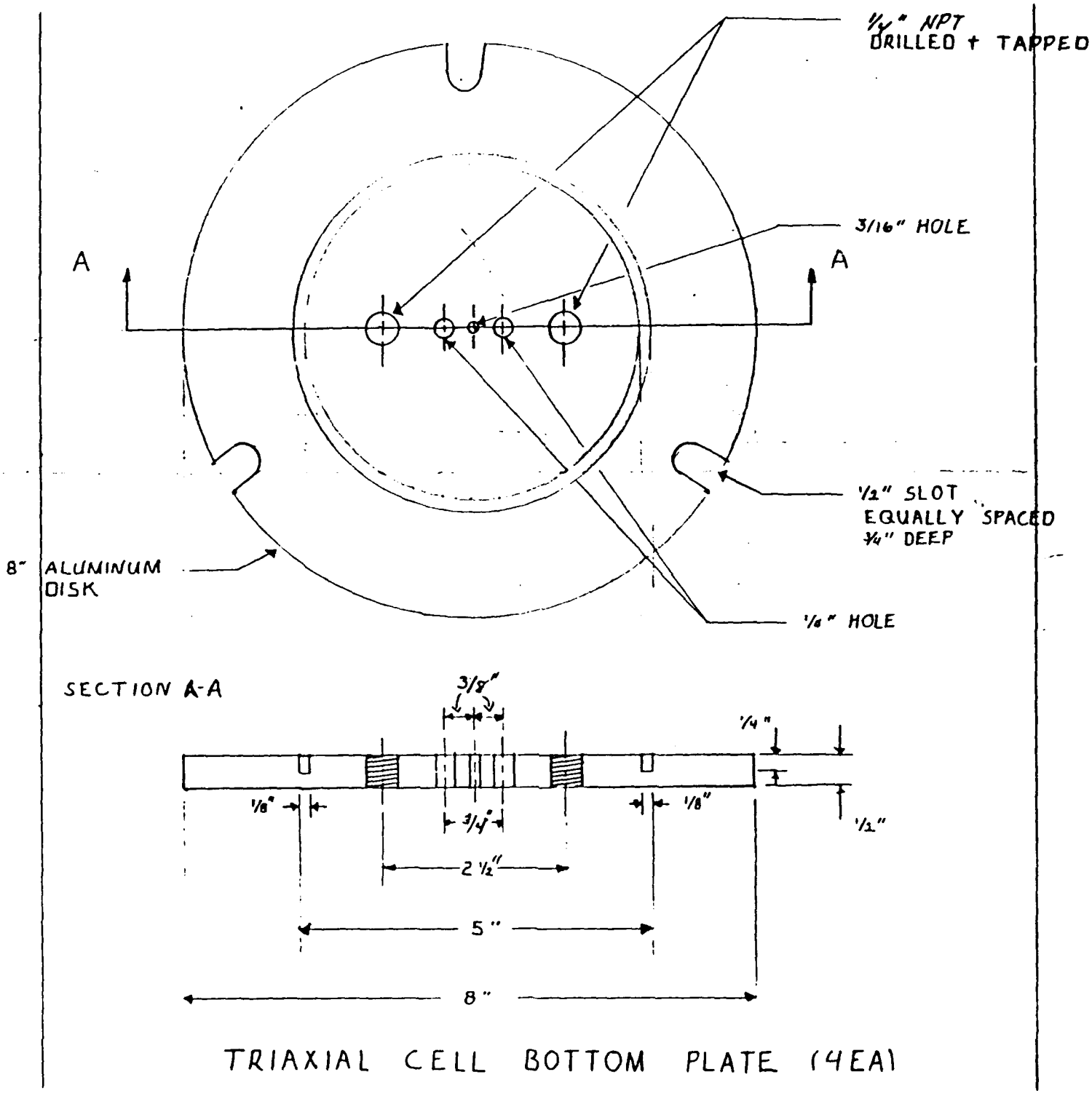
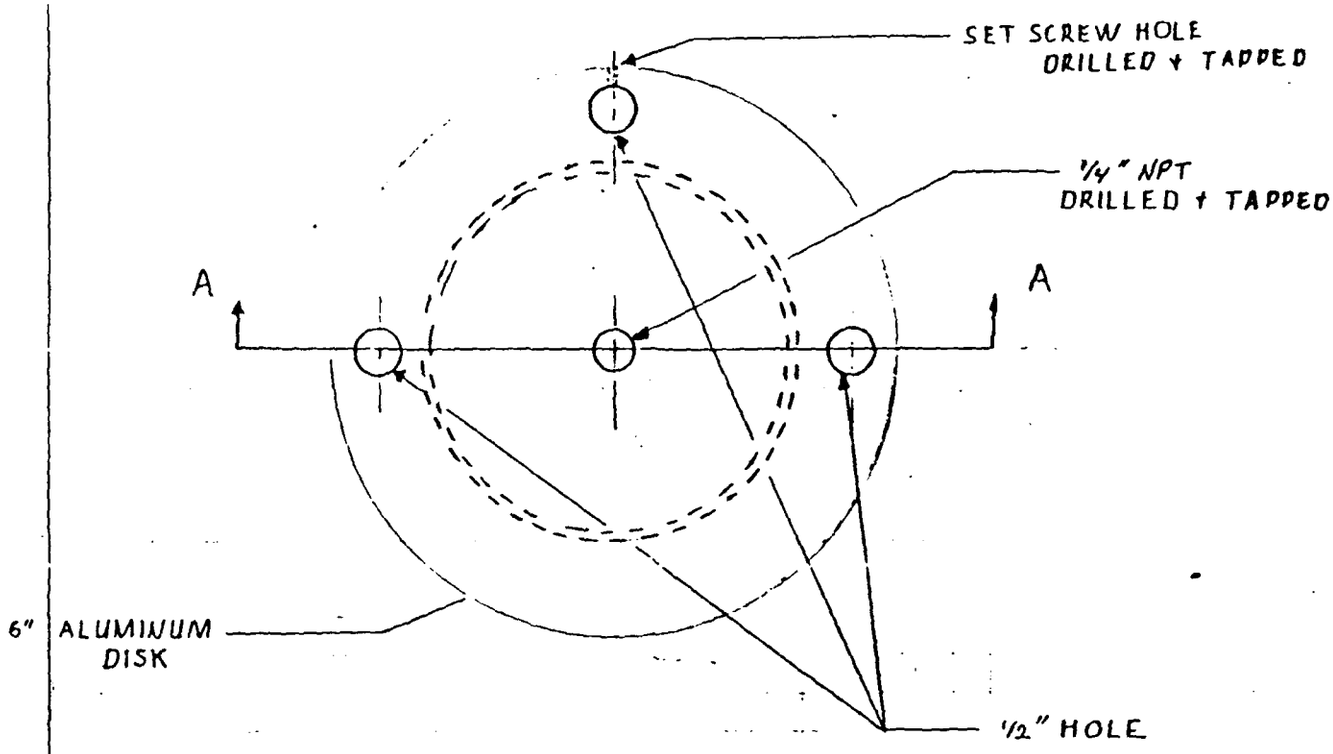
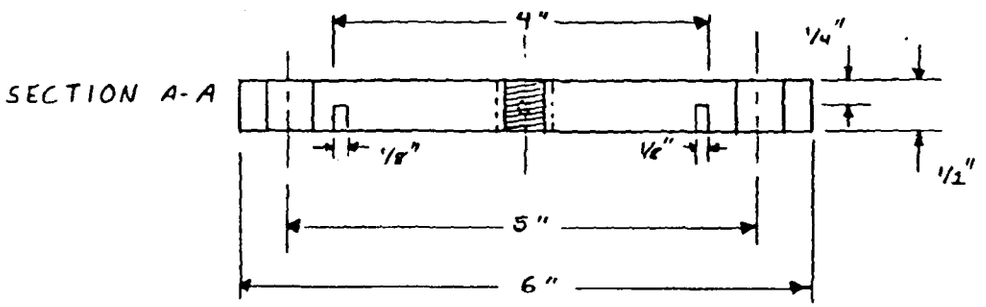


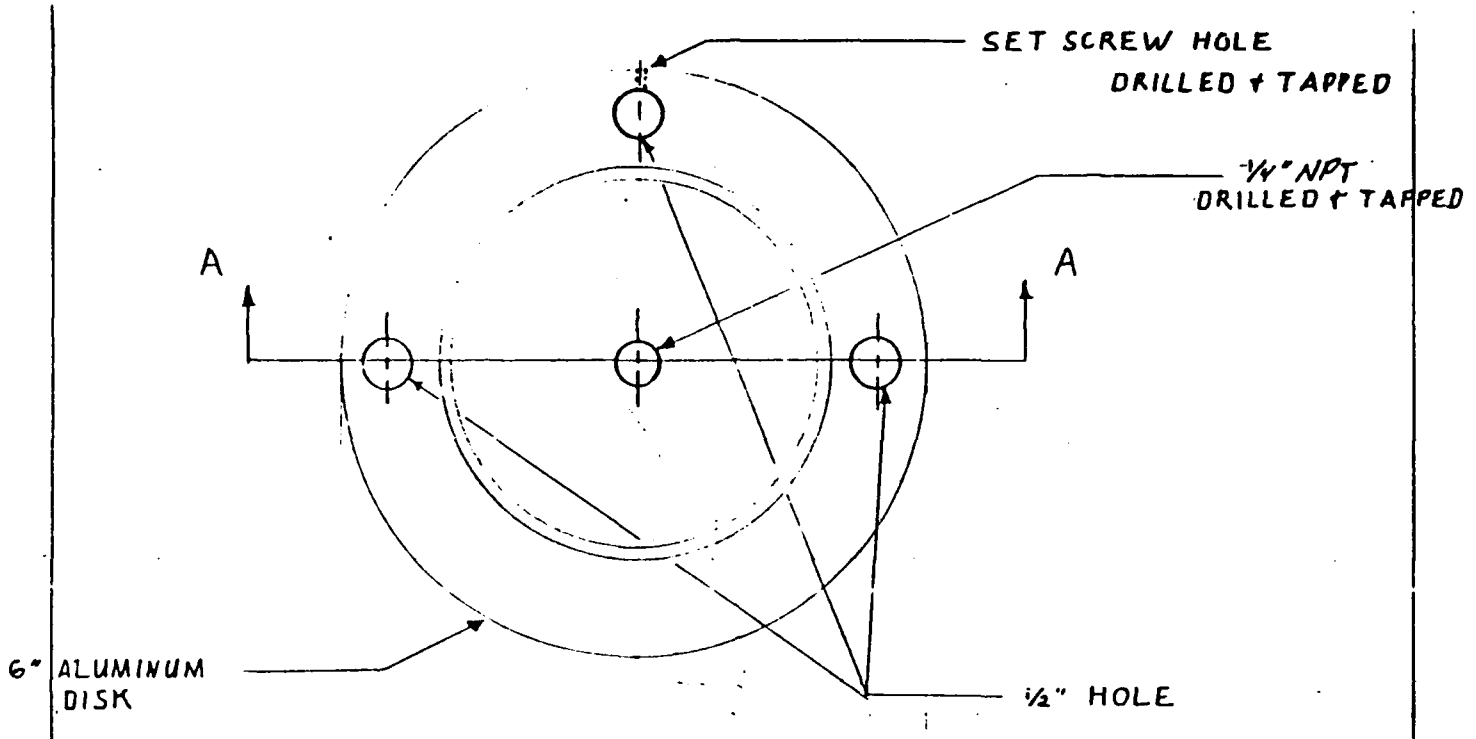
Figure B-4: Test Cell Bottom Plate

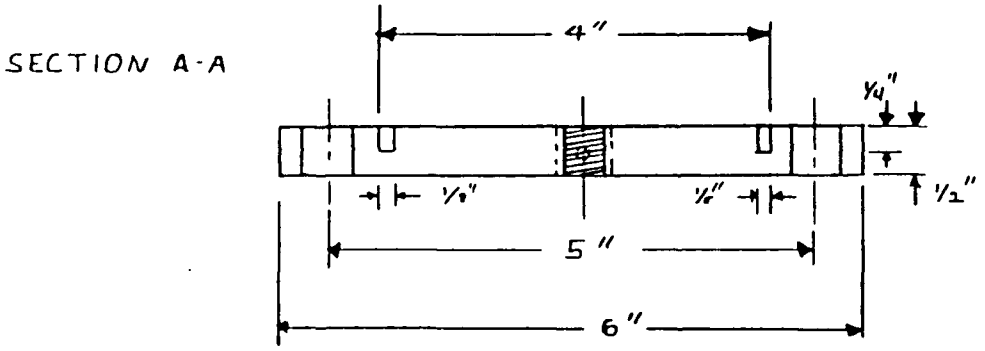




INFLUENT/EFFLUENT RESERVOIR TOP PLATE (13 EA.)

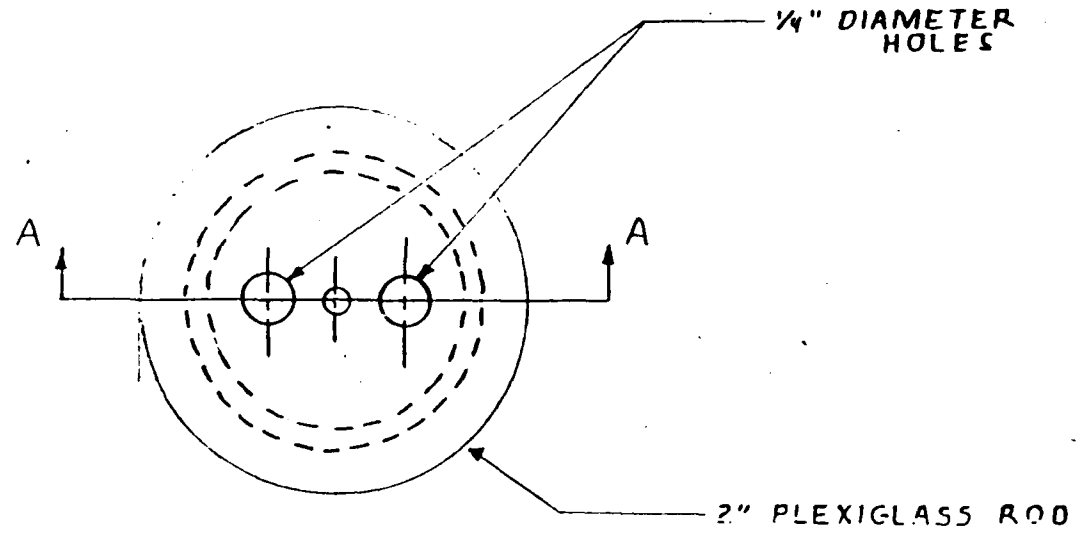
Figure B-5: Influent/Effluent Reservoir Top Plate





INFLUENT/EFFLUENT RESERVOIR BOTTOM PLATE (13 EA.)

Figure B-6: Influent/Effluent Reservoir Bottom Plate



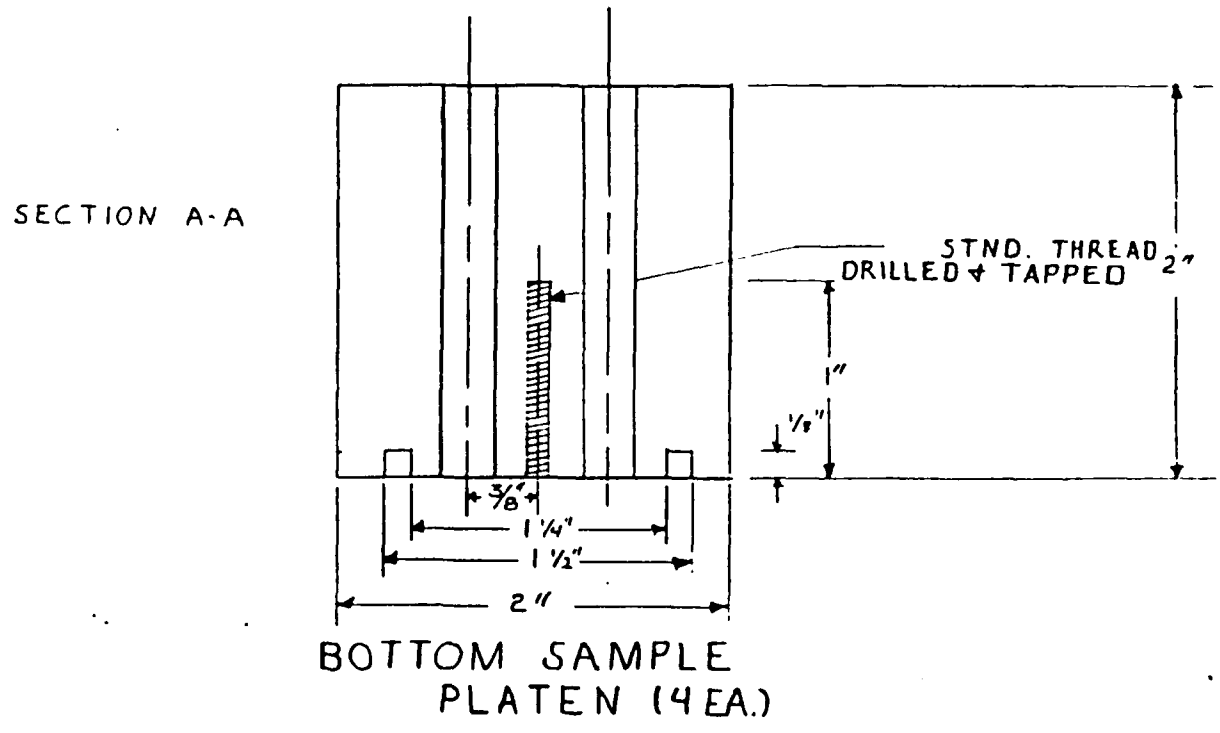
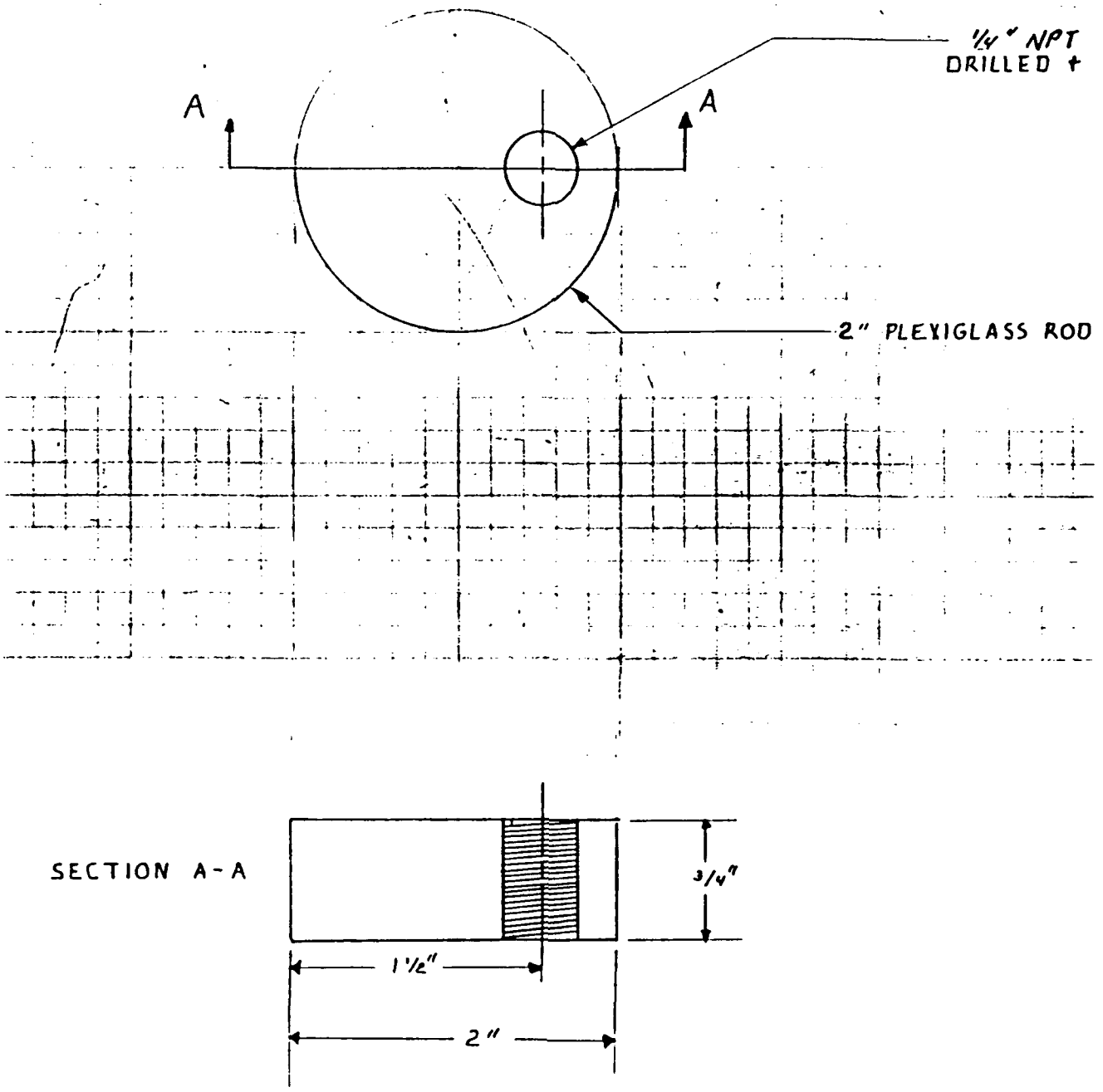


Figure B-7: Bottom Sample Platten



TOP SAMPLE
PLATEN (4 EA.)

Figure B-8: Top Sample Platten

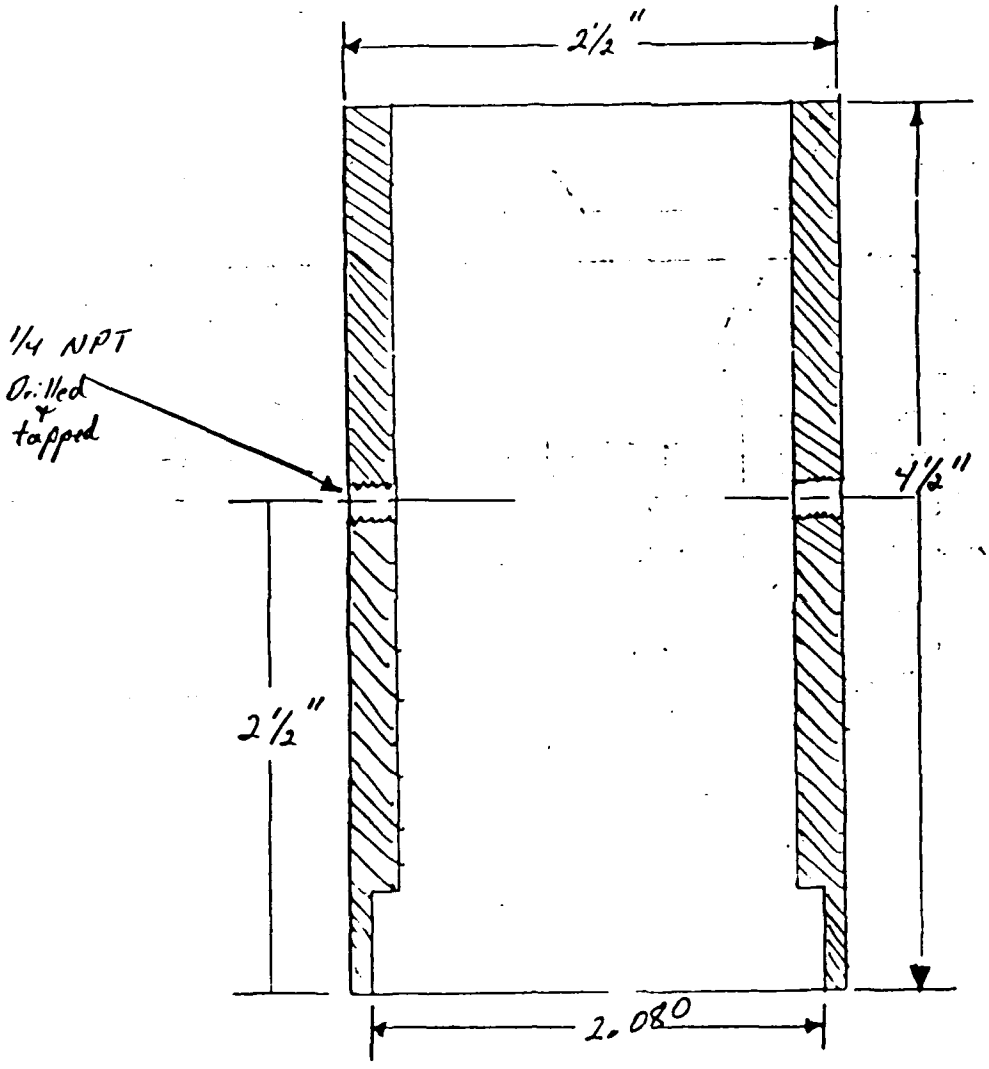


Figure B-9: Membrane Stretcher

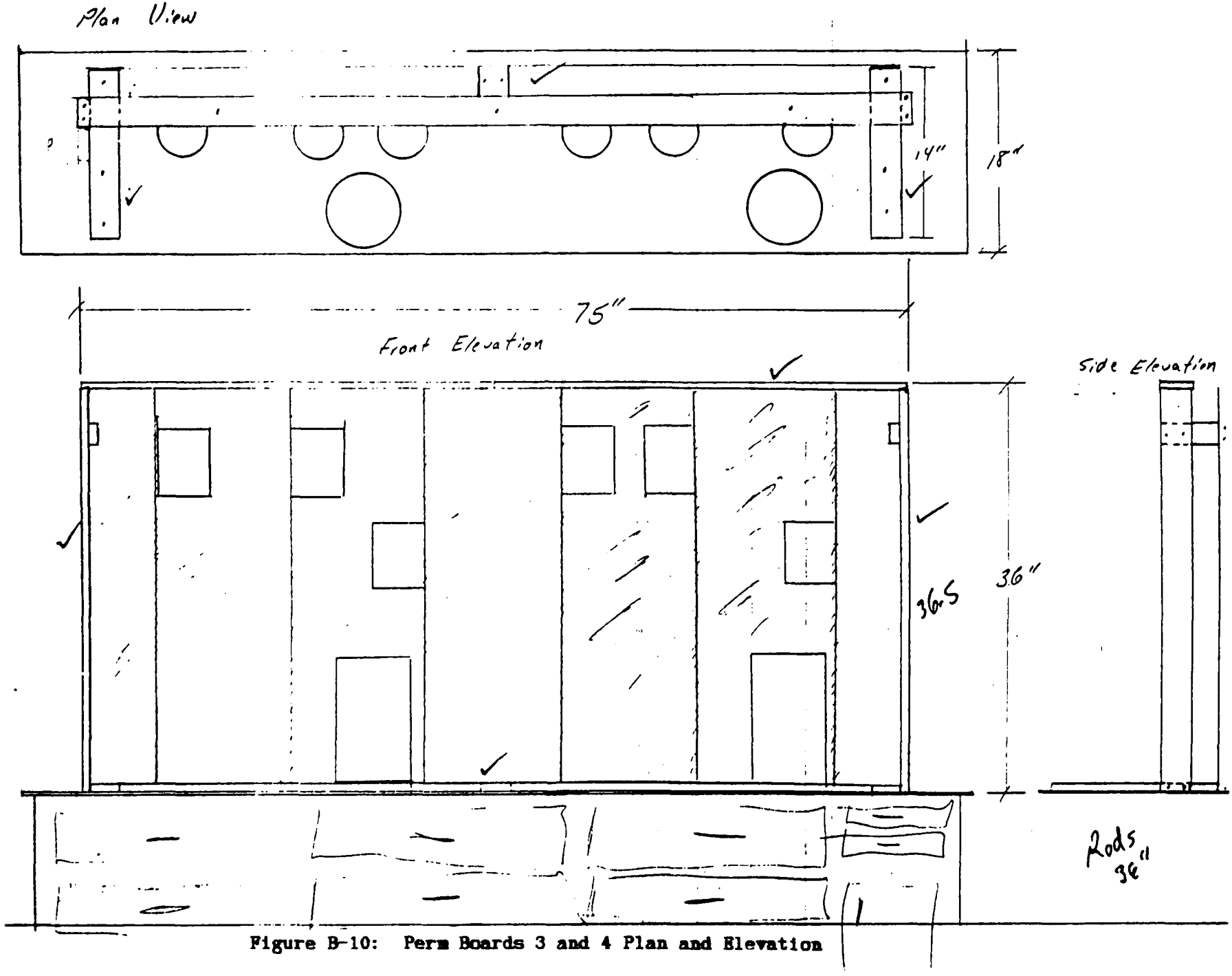


Figure B-10: Perm Boards 3 and 4 Plan and Elevation

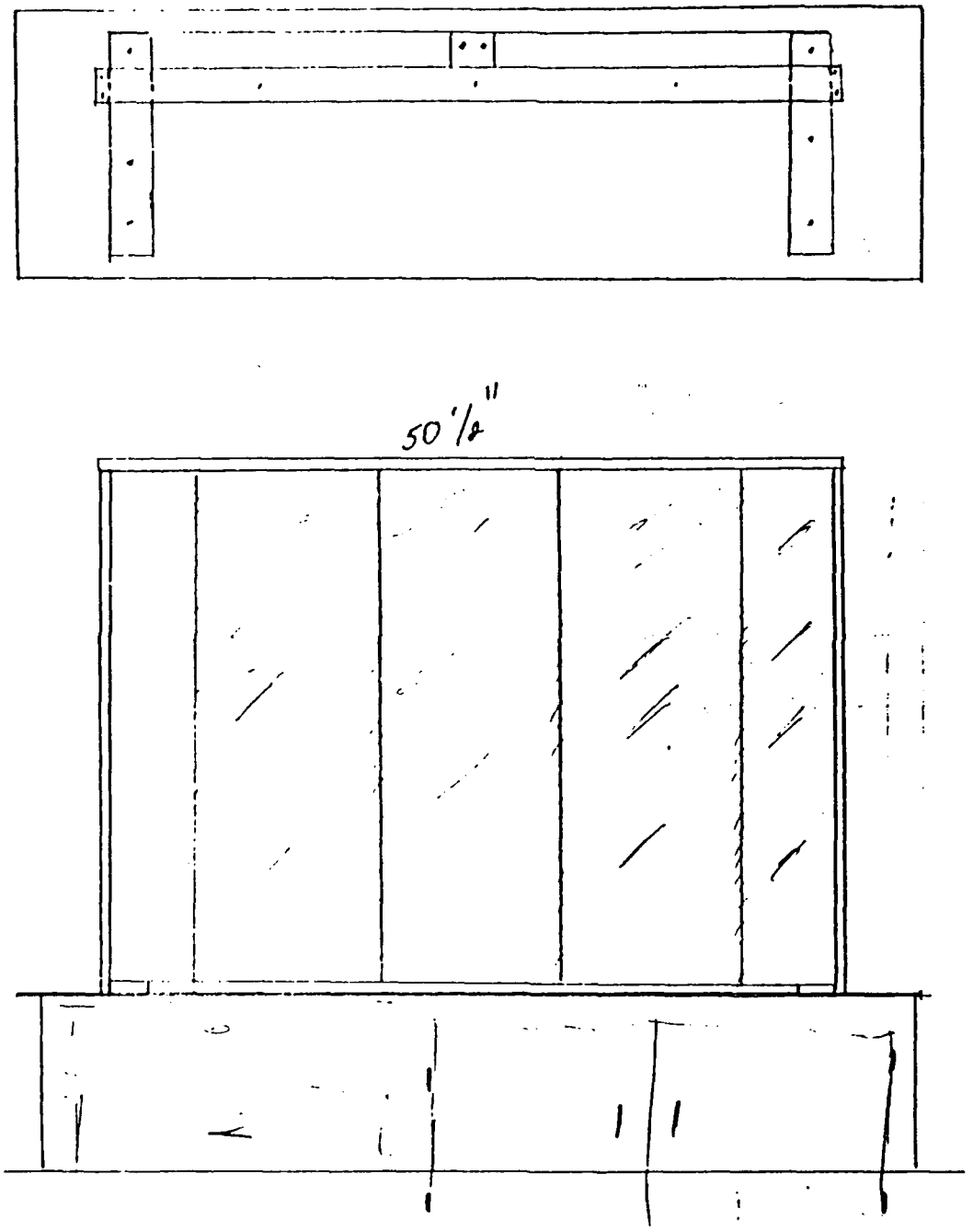


Figure B-11: Perm Board 1 Plan and Elevation

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